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ON THE

PROGRESS OF CHEMISTRY.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1904.

ISSUED BY THE CHEMICAL SOCIETY.

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INTRODUCTION.

THE issue of a systematic series of reports in English on the progress of chemistry in its several divisions and applications has long been desirable, but a definite scheme was not formulated until April last, when the Council of the Chemical Society adopted a resolution that such reports should be prepared for the year 1904, and continued annually. The division of the subject under the same headings as those adopted for the classification of the Abstracts published in the Chemical Society's Journal was thought convenient, but the large extent of matter to be dealt with made it necessary further to divide the work of reporting on the department comprised under the title of "Organic Chemistry," while it was thought probable that in future years a similar subdivision of "General and Physical Chemistry" would become necessary. An additional article referring to the history and development of the new subject of "Radioactivity" has also been prepared.

The object of these "Reports" is to present an epitome of the principal definite steps in advance which have been accomplished in the preceding year, for the benefit of all workers, students, or teachers of chemistry, or those chemists who are engaged in technical or manufacturing applications of chemistry, in order that specialists in any one department of the science may obtain without difficulty information as to the nature and extent of progress in other branches of the subject to which they have not paid special attention.

With these objects in view, the Council invited a number of gentlemen, distinguished for their acquaintance with the several divisions of the subject already indicated, to prepare Reports, and their names attached to the several articles afford a guarantee that the work has been done carefully, judiciously, and accurately.

Obviously, the selection of matter from so large a field involves the apparent neglect of some subjects, but it is believed that in the several

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Reports nothing has been omitted which can be regarded as of fundamental importance.

It must further be added that inasmuch as no Report can be finished by the author before December 31st in each year, and in a few cases it will necessarily be somewhat later, the Reports cannot be in the hands of the Fellows of the Society till the early Spring, though it is to be hoped that they may be ready some time before the Anniversary Meeting.

W. A. T.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Agron.	Annales agronomiques.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
**Bied. Centr.*	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bihang K. Svenska Vet.-Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
**Chem. Centr.*	Chemisches Centralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett Harz Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Zeit.	Chemiker Zeitung.

* Abstracts from the *Centralblatt* are made only in the case of papers published in journals other than those included in this list.

Abbreviated Title.	Journal.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Fed. Inst. Brewing	Journal of the Federated Institutes of Brewing.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Milch Zeit.	Milch Zeitung.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. Scient.	Moniteur Scientifique.
Nuovo Cim.	Il Nuovo Cimento.
Öfver K. Vet.-Akad. Förh.	Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc.	Proceedings of the Chemical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.

Abbreviated Title.	Journal.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften in München.
Trans.	Transactions of the Chemical Society.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitth.	Tschermak's Mineralogische Mittheilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeit anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Farb. Text. Ind.	Zeitschrift für Farben- und Textil-Industrie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeit. prakt. Geol.	Zeitschrift für praktische Geologie
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeit. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

Elements and Compounds.

W. Ostwald, in his Faraday Lecture[1] on Elements and Compounds shows how it is possible to deduce from the principles of chemical dynamics the law of constant proportions, the law of multiple proportions, and the law of combining weights. For the mode of deduction, the original paper must be consulted, but the following points in the argument may receive mention here. A homogeneous system (or phase) may be of two kinds. It may be a hylotropic body, which retains its composition unchanged when it passes into a new phase (for example, water during evaporation), or it may be a solution which in general changes in composition when a new phase is formed (for example, by evaporation), and may be decomposed into several hylotropic substances. When a body remains hylotropic in its phases within a wide region of temperature and pressure, it is conceived to be a chemical substance or chemical species: hence the constant composition of chemical substances. Substances whose sphere of existence covers all accessible states of temperature and pressure are called elements; they are never other than hylotropic, and all other substances must be ultimately resolved into them. Let there be three elements A, B, C, forming the binary compounds AB, AC, BC and the ternary compound ABC. If these are the only substances formed from the three elements, and if ABC may be produced, firstly, by the combination of A and B to AB, which afterwards combines with C, and secondly, by the combination of A and C to AC, which then combines with B, it follows that the proportions in which A, B, and C exist in ABC are their combining proportions in the

[1] *Trans.*, 1904, **85**, 506.

binary compounds, and if we deduce the combining weights of B and C from their compounds with A, the weights so obtained will express their combining proportions with each other. If no compounds can be formed except according to the combining weights of the elements, the law of multiple proportions follows at once, as may be exemplified by substituting B for A in the above deduction.

The author then discusses briefly the nature of the elements. Matter may be defined as a complex of energies which we find together in the same place, and may be conceived as continuous in space. The difference between different chemical substances is a difference of their specific energy content (for example, specific volume, specific entropy). The elements have relative minima of available energy, and the difficulty (or impossibility) of passing from one element to another is due to the difficulty (or impossibility) of concentrating a sufficient amount of available energy in the given space to effect the transformation. When the relative minima are not well marked, the transformation may occur; thus radium may be resolved through other temporary elements into helium. Such transformations we should expect to occur with the liberation of enormous amounts of energy, a conclusion which finds confirmation in the behaviour of radium.

Structure of Atoms.

An electrical theory of the structure of the atom is put forward by J. J. Thomson.[1] He assumes an atom to consist of a large number of negative electrons in a sphere of uniform positive electrification. The negative electrons are arranged in concentric shells, and although the author has not yet succeeded in giving a complete mathematical treatment of the conditions of stability and the oscillation and rotation in these shells, he is able from a consideration of similar corpuscles arranged in concentric rings to indicate the characteristics of the systems. The results which he obtains for systems containing different numbers of corpuscles in their rings offer a very close analogy to the variation in the valency of atoms in the periodic system with ascending atomic weights, as the hypothetical electrical atoms group themselves with regard to stability in a periodic fashion with regular variation of electropositive and electronegative valencies as the number of corpuscles increases. The non-valent elements, helium and its congeners, find a natural place in the system, and the breaking up of the atoms of radioactive elements, with great liberation of energy, finds a satisfactory analogue in electrical atoms of many corpuscles (high atomic weight) arranged in the shells in groups.

[1] *Phil. Mag.*, 1904, [vi], **7**, 237.

Molecular Attraction.

J. E. Mills[1] in a paper on molecular attraction deduces the following formula on the assumption that the attraction varies inversely as the square of the distance and is independent of the temperature, and that the total energy *per se* of a molecule is the same in the liquid as in the gaseous state :

$$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant.}$$

In this formula, L is the total latent heat of vaporisation, E_1 the energy spent in overcoming external pressure, namely, $0{\cdot}0_4 31833\ P(V-v)$ cals., d and D the densities of liquid and vapour respectively. Of a total of twenty-one substances examined, the expression is constant for eleven, and for four the divergence may be accounted for by errors of observation. For five associating liquids, the constancy is not very good, but acetic acid is the only decided exception.

Exact Molecular Weights of Gases.

The determination of exact molecular weights generally consists in the determination by physical methods of an approximate value, which is then fixed accurately by means of the known atomic weights of the elements involved. Daniel Berthelot, on the assumption that perfect gases would obey Avogadro's Law and Gay-Lussac's Law of combining volumes with absolute accuracy, has calculated the exact molecular weights of several simple gases by taking into account the deviation of these gases from perfection, and from the molecular weights so obtained he has been able to assign values to the atomic weights of the elements of which the gases are composed. His latest results are given in connected form in *Zeit. Elektrochem.*, 1904, **10**, 621. He considers first the data for the weight of a litre of the various gases, then the deviation of the gases from Boyle's Law between 1 and 2 atmospheres at 16°. From the latter values, he calculates the deviations for 0° between zero pressure and one atmosphere for the more compressible gases by means of van der Waals's formula : for the incompressible gases, this correction for the different range of pressures is negligible. In this way he obtains a table of deviations from the laws of perfect gases $({}_0A_1)_{0°}$, and by multiplying the observed weight of a litre of the various gases at 0° by $1 - A$ he obtains the weight which the gases would have if they were perfect gases. Employing the ordinary molecular weight M, as deduced from the

[1] *J. Physical Chem.*, 1904, **8**, 383.

atomic weights, he obtains the following table of observed molecular volumes v_0 and of corrected molecular volumes V_0.

	M.	v_0.	$1-({}_0A_1)_0$.	V_0.
H_2.....	2·0152	22·4363	1·00064	22·4220
CO	28·004	22·4015	0·99954	22·4116
O_2.....	32·000	22·3970	0·99924	22·4140
CO_2	44·004	22·2657	0·99326	22·4167
C_2H_2.....	26·016	22·2227	0·99160	22·4109
HCl	36·458	22·2216	0·99210	22·3983
SO_2	64·06	21·8890	0·97642	22·4174

The numbers in the last column should be identical on the author's assumption. Using all available data, except those for nitrogen and its compounds, the author finds, as the mean value of the gram-molecular volume,

$$V_0 = 22{\cdot}412 \text{ litres.}$$

Nitrogen and nitrous oxide, when treated in the same way, yield $V_0 = 22{\cdot}46$ on the assumption that $N = 14{\cdot}04$. On the assumption that $N = 14{\cdot}005$, these two gases fall into line with the others. The author therefore concludes that the official atomic weight of nitrogen deduced from the experiments of Stas is too high.[1]

By analogous reasoning, Guye [2] comes to a similar conclusion, the values of the atomic weight of nitrogen deduced by him being 14·004. Direct experiments on the atomic weight of nitrogen from the reduction of nitrous oxide by metallic iron have yielded in his hands the value 14·01 as maximum.[3]

Ramsay and Steele [4] endeavoured to obtain exact molecular weights in D. Berthelot's sense by extrapolation from vapour density determinations of liquid substances at low pressures. They found, however, considerable discrepancies between the values calculated from the atomic weights and the values which they obtained. M. Reinganum [5] has developed an equation of state for feebly compressed gases, and has calculated from Young's observations on *iso*pentane a satisfactory molecular weight for that substance. Applying the same equation to Ramsay and Steele's observations, he finds for seven liquids a molecular weight which does not differ by as much as 0·2 per cent. in the worst case from the molecular weight calculated from the formula. The average divergence is less than 0·1 per cent.

[1] Compare Rayleigh, *Proc. Roy. Soc.*, 1904, **73**, 154.
[2] *Compt. rend.*, 1904, **138**, 1213. [3] *Ibid.*, 1494.
[4] *Phil. Mag.*, 1903, [vi], **6**, 492.
[5] *Zeit. physikal. Chem.*, 1904, **48**, 697.

Gas Constants.

In connection with Daniel Berthelot's determination of the theoretical value of the gram-molecular volume, W. Nernst [1] gives the following values for the gas-constant in different units. In these calculations, it is assumed that the absolute zero is $-273{\cdot}09°$, that 10^7 erg $= 0{\cdot}23872$ gram.-cal., and that the unit electrochemical charge, or faraday, is 96,540 coulombs for the gram-equivalent.

$$\begin{aligned} R &= 0{\cdot}83155 \times 10^8\,[\text{erg} \times T^{-1}]. \\ &= 8{\cdot}3155\,[\text{joule} \times T^{-1}]. \\ &= 0{\cdot}082068\,[\text{litre-atmosphere} \times T^{-1}]. \\ &= 1{\cdot}98507\,[\text{gram-cal.} \times T^{-1}]. \\ &= 0{\cdot}86134 \times 10^{-4}\,[\text{volt-faraday} \times T^{-1}]. \end{aligned}$$

The last value is the "electrolytic gas-constant," used in calculations of *E.M.F.* In terms of it and the ionic concentrations, the usual expression for the electromotive force becomes

$$E = \frac{0{\cdot}057732}{n} \log_{10} \frac{C}{c} \text{ volt},$$

n being the electrovalency.

Taking the weight of a litre of air at 0° as 0·001293 gram, we have for the molecular weight (M) of a gas in terms of its density referred to air as unity (Δ):

$$\begin{aligned} \text{M} &= 0{\cdot}001293 \times 22412\,\Delta = 28{\cdot}979\,\Delta \\ &= 29\,\Delta \end{aligned}$$

with close approximation.

Valency and Molecular Compounds.

A theory of valency and of molecular compounds is propounded by R. Abegg.[2] He defines stable substances as the products of reaction between substances with extremely great reciprocal affinity. Such substances do not in general exist: ordinary stable compounds may be regarded either as containing in a homogeneous system the proximate constituents from which they were formed, or into which they may decompose, or as having separated out as a new phase from such a homogeneous system. Phosphorus pentachloride may be taken as a well-marked example of such a substance. Labile compounds, on the other hand, are not strictly speaking in equilibrium with their possible products of decomposition, and only exist on account of the decomposition occurring with extreme slowness. Thus potassium chlorate is in

[1] *Zeit. Elektrochem.*, 1904, **10**, 629.
[2] *Zeit. anorg. Chem.*, 1904, **39**, 330.

this sense unstable, although at a low temperature no perceptible decomposition into potassium chloride and oxygen occurs. The difference between these classes is ultimately only one of degree.

The valencies of any one element are regarded by the author as differing in intensity, and unstable compounds may be expected to be formed of those elements which do not in general exert all their valencies. Looking at the various elements as presented in the periodic system, we find good grounds for assuming that each has a maximum valency, but that the valency exerted in any one compound depends on the nature of the atom or radicle with which the element combines. Along with chemical valency, in the ordinary sense, must be considered electrochemical valency, which is generally less than the maximum valency, and of essentially polar character, thus affording a clue to the nature of valency in general. For each element, the author assumes two kinds of valency of opposite polarity: normal valencies and contravalencies. The normal valencies are the stronger, and are positive for metals, negative for non-metals. The sum of the valencies and contravalencies for each element is 8, their distribution amongst the periodic groups being as in the following table:

Group	1.	2.	3.	4.	5.	6.	7.
Normal	+1	+2	+3	±4	−3	−2	−1
Contra	(−7)	(−6)	(−5)		+5	+6	+7

The maximum normal valency is occasionally not exerted; the contravalencies are very frequently latent. In a periodic group, the contravalencies become more active the higher the atomic weight of the element; thus in the halogens the seven positive contravalencies are most marked in the case of iodine. Since we know from a study of cathode rays that positive electrons are more closely associated with matter than negative electrons, we might expect that the positive contravalencies of the negative elements should be more evident than the negative contravalencies of the positive metals. The author explains the monatomic character of the molecule of a metal as contrasted with the polyatomic character of the non-metallic molecule by the weakness of the contravalencies in the first instance. Complex ions formed by the addition of a neutral molecule to a negative ion (for example, AgI,I') are much more numerous than those formed from a neutral molecule and a positive ion, thus, AgI,Ag_2''. Here the contravalencies are again supposed to be active, more so for the negative than for the positive elements.

Molecular compounds may be classified provisionally into those whose component molecules are alike, and those whose component molecules are unlike. In the first class (associated molecules), if we are to attribute the association to chemical forces of the ordinary type,

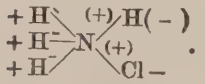
we must assume that the maximum valency of at least one of the component elements is not reached in the non-associated molecules, and therefore we may expect one element at least to belong to the higher groups of the periodic system. This expectation is realised in such molecules as H_2O, NO_2, P_2O_3, As_2O_3, SO_3, HF, $AlCl_3$, $FeCl_3$, hydroxylic organic compounds, oximes, and aldehydes. Similarly, we may expect the same elements to be present in "molecular compounds" in the ordinary sense. Of these, very few exist in the gaseous state, but the following may be taken as instances: $(CH_3)_2O,HCl$; PCl_3,Cl_2; ICl,Cl_2; NH_3,HCl. Molecular compounds in the solid state are of frequent occurrence, for example, hydrates, ammoniates, alcoholates, hydroperoxide compounds, the double chlorides of $AuCl_3$, $PtCl_4$, $SnCl_4$, with SCl_4, PCl_3, NOCl, &c. Since in each of these we have elements of the required type, it is unnecessary to assume special "crystallographic forces" to account for the existence of these solids. Some of these solid molecular compounds persist when in solution, for example, chloral hydrate in acetic acid, anthracene picrate in alcohol. Solutions may be regarded as molecular compounds of solute and solvent when the act of dissolution is accompanied by the usual indications of chemical action, such as thermal effect and change of volume. These changes are most marked when the substances contain elements of high but not fully satisfied valency. If both solvent and solute have latent valencies, the solvent, according to the law of mass action, will work against the association which the solute would exhibit by itself, or dissolved in a solvent without latent valencies such as a saturated hydrocarbon. This conclusion accords well with observed facts. In electrolytic solutions, the author postulates the following equilibria:

1. Ion + ion $\rightleftarrows$ undissociated molecules.
2. Ion + solvent $\rightleftarrows$ compound of ion with solvent.
3. Undissociated molecules + solvent $\rightleftarrows$ compound of undissociated molecule with solvent.

Feebly dissociating solvents are those which have no great tendency to combine with ions (2). If the tendency to ionisation (1) is well developed, the affinity of the undissociated substance for the solvent (3) is unimportant, as the non-ionised substance will not reach a high concentration compared with the ions. This case is represented by the solutions of strong electrolytes, whose solubility is therefore determined essentially by the affinity of the ions for the solvent, and is consequently great in water compared with the solubility in feebly dissociating media. The substances found by Walden and Centnerszwer to be soluble in liquid sulphur dioxide readily react with the solvent. It has been shown that anions such as iodide, bromide, and thiocyanate combine partially with sulphur dioxide in aqueous

solution, and it has been found that the alkali salts with these anions dissolve well in liquid sulphur dioxide giving conducting solutions (2).

A diagram of the variation of electro-affinity in the periodic system is given by the author, the data being derived from potential measurements and general chemical behaviour. The members of the eighth group receive special discussion, which is also accorded to carbon, whose varying polarity is held to account, partially, at least, for the variety of its compounds. The views of the author with regard to the distribution of valencies in ammonium chloride may best be illustrated by means of the following diagram, contravalencies being enclosed in brackets :



The fourth hydrogen is here supposed to be united to the nitrogen atom by means of the comparatively feeble contravalencies. When hydrocarbon radicles are substituted for hydrogen, the combination is much firmer on account of the carbon valency being much more powerful than the positive contravalency of hydrogen. Thus the tetra-alkyl-ammonium salts are comparatively stable.

Atomic Volume and Cohesion.

T. W. Richards [1] continues his investigation of the significance of change in atomic volume. Proceeding on his assumption of an atom compressible by physical and chemical attraction, he deduces the result that a given affinity will produce a greater contraction (reduction of atomic volume) the more compressible the element (atom) is. This result is verified for the halogens and the alkali metals on the assumption that the heat of formation of the compounds considered is proportional to the work of affinity. The effect of the chemical pressure is sometimes obscured by the effect of physical pressure (cohesion), and thus exceptions to the above rule may occur. As a measure of cohesion, the author takes non-volatility. Of two comparable substances, the less volatile has the smaller molecular volume. The expansion on the inversion of tin by cooling is accounted for by the smaller cohesion of the grey variety. A comparison of many organic isomerides shows that the less volatile substance is the denser and less compressible. Molecular volumes are only additively composed of the atomic volumes when liquids are compared, not at the same temperature, but at their boiling points, when the effect of cohesion is equalised.

[1] *Zeit. physikal. Chem.*, 1904, **49**, 15.

Effect of Specific Heat on Equilibrium.

In his study of the relation between the change of atomic volume on interaction and the chemical affinity of the reacting substances, T. W. Richards[1] came to the conclusion that during a chemical action, unaccompanied by change in concentration, the heat developed by the action is greater than, equal to, or less than the change of free energy, according as the heat capacity of the system before the action is greater than, equal to, or less than the heat capacity of the system after the reaction. With reference to Richards's work, van't Hoff has developed the following equation for the change in free energy during reaction.[2] If E is the change in free energy at the temperature T, E_o that at the absolute zero (which is equal to Q_o, the heat evolved at that temperature), S the difference $S_A - S_B$ of the specific heats of the system before (S_A) and after (S_B) the transformation, and A an integration constant, then

$$E = E_o + AT - ST\log_e T.$$

It is assumed in the integration that S does not change with the temperature, although S_A and S_B may. The free energy appears to be made up of three terms, the second of which refers to changes of concentration. This term vanishes when there is no change in concentration, and then

$$\frac{dE}{dT} = -S(1 + \log_e T),$$

a relation identical with that of Richards. For the ordinary temperature, $1 + \log_e T = 6{\cdot}7$. In transformations such as fusion, or the passage of one allotropic phase into another, the term AT, although small, cannot be altogether neglected.

The author shows that when S is not equal to zero, the curve of the variation of the free energy with temperature must intersect the curve of the variation of the heat of reaction with temperature at two points, first at the absolute zero, and secondly at a temperature where the free energy curve is at a maximum or minimum. Since in an inversion (condensed equilibrium) E becomes zero at the inversion temperature, S must be positive, and $S_A > S_B$, that is, the substance which is stable at the higher temperature has the greater specific heat, for heat is always evolved in passing from the substance stable at the higher temperature to that stable at the lower. Thus the specific heat of liquids must be greater than that of the solids from which they are derived, that of monoclinic sulphur greater than that

[1] *Zeit. physikal. Chem.*, 1902, **42**, 129.
[2] Boltzmann, *Festschrift*, 1904, p. 233.

of rhombic sulphur, &c. The following table of specific heats illustrates this rule. Under S_A the specific heat of the substance is stable at the higher temperature, under S_B the specific heat of the substance is stable at the lower temperature.

	S_A.	S_B.
Carbon	0·114° (graphite at −50°)	0·063° (diamond at −50°)
,,	0·467 (,, 1000°)	0·459 (,, 1000°)
Phosphorus	0·18 (yellow)	0·17 (red)
Sulphur	0·19 (monoclinic)	0·16 (rhombic)
Tin	0·56 (ordinary)	0·55 (grey)
Silver iodide	0·0577	0·0544
Potassium nitrate	0·285	0·203
$Na_2S_2O_3,5H_2O$	0·569 (fused)	0·445 (solid)

That the specific heat of a liquid is greater than that of the corresponding solid is a well-established fact.[1]

Since in the equation

$$E = Q_o + AT - ST\log_e T$$

E and Q coincide at the absolute zero ($T=0$), Q determines at that point the sense in which a chemical action will occur. At ordinary low temperatures, T is still comparatively small, and Q still determines in general the sense of the reaction (Berthelot's Third Principle, Julius Thomsen's principle that purely chemical action is always accompanied by evolution of heat). It is only at high temperatures that exceptions to this principle become numerous.

The displacement of equilibrium by rise of temperature according to a former generalisation of the author always takes place in such a manner that the system formed by heat absorption is produced. The above equation shows, however, that this is not the case unless S has a positive value, and thus at high temperatures reactions will only be accompanied by heat absorption when the heat capacity of the products of the reaction is greater than that of the reacting substances. This new condition explains a whole group of facts. In the case of gaseous dissociations, that is, a class of actions which at high temperature are the reverse of those occurring at lower temperatures, it is by no means always the case that they occur with absorption of heat, although this is evidently a condition. They are rather such transformations as, owing to decomposition, produce a greater number of gaseous molecules, and thus a system having a higher specific heat than the original system.

Atomic Heat.

In connection with the atomic heats of the elements, it may be noted that W. A. Tilden has proved experimentally[2] that some elements

[1] Compare W. A. Tilden, *Phil. Trans.*, 1904, **203** A, 147.

[2] *Ibid.*, 139.

which show in the uncombined state great variability of specific heat with the temperature retain this variability in many of their compounds. Thus Neumann's law that the molecular heat of a compound is equal to the sum of the atomic heats of its constituent elements holds good for these variable elements at all temperatures.

Osmotic Pressure.

The Earl of Berkeley and E. G. J. Hartley describe an apparatus for the direct measurement of high osmotic pressures.[1] The values which they obtained for concentrated solutions of cane sugar (120—420 grams per litre) are greatly above those deduced from Boyle's law, and in moderately close agreement with the osmotic pressure values of H. N. Morse and J. C. W. Frazer[2] and the cryoscopic measurements of Arrhenius and others.[3]

J. Šebor[4] has observed that the rate of flow of water through a semipermeable membrane is proportional to the difference of osmotic pressure of the fluids on the two sides of the membrane. The rate of diffusion through the membrane increases rapidly with rise of temperature.

Colloidal Solutions.

The subject of colloidal solutions still receives much attention. A valuable alphabetic bibliography is given by A. Müller.[5] Discussion practically centres round the question whether such solutions consist of one phase or of two. On the former assumption, they differ in no way except in degree from solutions proper; on the second assumption, they are essentially different, and the conceptions of ordinary solutions, with the results deduced from these conceptions, are not applicable to colloidal solutions at all. In favour of the first view, a great many facts are marshalled by E. Jordis.[6] The author conceives the state of a colloidal solution to be a complex homogeneous equilibrium amongst a great number of dissolved substances, some of which are present in very small quantity. No hydrosol has been prepared in a pure state, the small amounts of so-called "impurities" in the solution being necessary conditions for the homogeneous equilibrium. When they are removed, the hydrosol is precipitated (gelatinises or coagulates). The almost negligible depression of freezing point, &c., is accounted for by the sparing solubility and the magnitude of the dissolved molecule.

F. G. Donnan[7] considers the possibility of accounting for colloidal

[1] *Proc. Roy. Soc.*, 1904, **73**, 436.
[2] *Amer. Chem. J.*, 1902, **28**, 1.
[3] Compare H. C. Jones and F. H. Getman, *Zeit. physikal. Chem.*, 1904, **49**, 454.
[4] *Zeit. Elektrochem.*, 1904, **10**, 347.
[5] *Zeit. anorg. Chem.*, 1904, **39**, 122.
[6] *Mon. Scient.*, 1904, [iv], **18**, 797.
[7] *Zeit. physikal. Chem.*, 1904, **46**, 197.

solutions as biphasic systems from the standpoint of the theory of capillarity. A mathematical discussion of the conditions for the existence of a negative surface tension is given. These conditions being fulfilled, two phases in contact would spontaneously intermingle in a state of very fine division. If the substances were such that one was highly mobile and the other highly viscous, the "solution" of the former in the latter would have high viscosity, whereas the "solution" of the latter in the former would possess considerable mobility. Here there is an analogy to colloidal jellies on the one hand, and to colloidal solutions on the other. The author considers the view that colloidal solutions are monophasic to be unsatisfactory, inasmuch as it still leaves unexplained the formation of the large molecular aggregates which it postulates. Further, many well-ascertained facts are at variance with it, for example, the non-existence of saturated solutions of colloids, the instability of their solutions, and their precipitation by electrolytes.

W. Ramsden[1] has found that many colloidal solutions (including all proteids investigated) and a number of fine and coarse suspensions (for example, flowers of sulphur in water) have the property that, quite apart from evaporation, solid or highly viscous coatings are spontaneously formed on the free surfaces of the solutions. These coatings are extremely delicate and fragile, but by purely mechanical processes they may be heaped up to form visible masses in many colloidal solutions, the masses in some instances being coagulated and thus rendered insoluble in the original liquid. Some, however, still remain "soluble" in the liquid. This behaviour is apparently not observed in the case of crystalloids proper, although it is exhibited by some, for example, ferric acetate, which are hydrolysed in aqueous solution with production of a colloidal hydroxide or basic salt. The observations then on the whole point to the analogy of colloidal solutions with suspensions, and not with solutions in the ordinary sense.

Fluid Crystals.

Fluid crystals are regarded by Tammann as suspensions or emulsions of one substance in another, a view which is not shared by Lehmann or by Schenck, who look upon them as homogeneous liquids. Various attempts have of late been made to decide between these conceptions. Thus, A. Coehn[2] and G. Bredig and Schukowsky[3] have investigated fluid crystals to find evidence of electric cataphoresis, which ought to be perceptible if the emulsion hypothesis is correct. The results obtained were negative. A. C. de Kock[4] has studied mixtures of fluid

[1] *Proc. Roy. Soc.*, 1904, **72**, 156.
[2] *Zeit. Elektrochem.*, 1904, **10**, 856.
[3] *Ber.*, 1904, **37**, 3419.
[4] *Zeit. physikal. Chem.*, 1904, **48**, 129.

crystals with each other and with foreign substances from the point of view of the phase rule, and finds that the liquid crystals do not differ from ordinary liquid phases and always act as monophasic systems. Optical experiments led him to the same conclusion, so that up to the present time there is no definite evidence that fluid crystals are other than homogeneous, apart from the turbid appearance which they present.

Dynamic Isomerism.

A method for the detection of dynamic isomerism in liquids has been proposed by R. Schenck and E. Ellenberger.[1] Ramsay and Shields have shown that the variation of molecular surface energy of different non-associating liquids with the temperature is diagrammatically represented by a series of parallel straight lines. Suppose now a non-associating substance exists in two forms, *A* and *B*, and that the proportions of these in the liquid state vary from temperature to temperature, as must be the case if the conversion of one into the other is attended with heat change. To each pure form on the diagram will correspond its own straight line, and the actual variation of the surface energy with the temperature for all the equilibrium mixtures will be a curve joining these two straight lines as asymptotes. This curve will show a maximum or a minimum temperature-coefficient according as the transformation on heating is into the form having a higher or lower critical temperature. Experiments with dibenzoylacetone show temperature-coefficients varying from 2·04 to 4·6 as maximum. Acetylacetone, on the other hand, shows a minimum of 1·64. Ethyl acetoacetate up to 140° behaves practically as a simple substance and not as a mixture of isomerides.

T. M. Lowry and W. Robertson[2] use solubility determinations for estimating the proportions of dynamic isomerides in solution.

A comprehensive survey of the subject of dynamic isomerism has recently been compiled by Lowry.[3]

Reaction Velocity in Heterogeneous Systems.

A theory of reaction velocity in heterogeneous systems has been put forward by Nernst.[4] Many facts lead to the assumption that equilibrium at the actual surface of contact between two phases is reached with great rapidity. The propagation of the action throughout the bulk of the phases, and therefore the velocity of the action between them, will thus be largely a question of velocity of diffusion. Noyes and Whitney have applied this principle to the study of the rate of dissolution

[1] *Ber.*, 1904, **37**, 3443.
[2] *Trans.*, 1904, **85**, 1541.
[3] *Brit. Assoc. Reports*, 1904, 1—32.
[4] *Zeit. physikal. Chem.*, 1904, **47**, 52.

of a solid, the rate being in this case dependent on the rate of diffusion of the dissolved substance, from the layer of saturated solution which is in contact with the solid, into the bulk of the solvent. Applying the same principle to the action between a solid, for example, magnesia, and a solution, say of hydrochloric acid, in which the solid dissolves, the author conceives the process as follows. Magnesia dissolves in the layer of liquid in contact with it, forming a feebly alkaline saturated solution of magnesia. Hydrochloric acid diffuses into this layer and neutralises the dissolved magnesia, which is instantaneously renewed by the dissolution of fresh solid. The rate, then, at which the magnesia dissolves is dependent on the rate at which the hydrochloric acid diffuses into the layer immediately in contact with the magnesia. With mechanical mixing, the rate is of course greatly increased. In this case, the bulk of the solution may be presumed at any one time to have the same concentration, the whole diffusion being supposed to take place through a very thin layer in the immediate neighbourhood of the solid, which will vary in thickness from case to case with the rate of stirring. It is a simple matter to give mathematical expression to this theory, which is applicable also to such reactions as electrochemical oxidations and reductions; and the conclusions to which it leads have been tested experimentally by E. Brunner.[1] Since the rate of reaction in an instance such as that above described is really dependent on the rate of diffusion of the dissolved acid, the nature of the solid undergoing dissolution should have little effect on the speed of dissolution. In agreement with this, Brunner found that metallic magnesium, magnesium oxide, and basic magnesium carbonate all dissolve, under like conditions, at practically the same rate in benzoic acid solution, and, further, that this rate agrees roughly with the rate of dissolution of benzoic acid in water, which depends on the same velocity of diffusion. Again, the rate of dissolution of solid iodine in water is about 75 per cent. of the rate of reduction of iodine in aqueous solution at a platinum cathode.

Nernst draws attention to the circumstance that on the above theory the application of van't Hoff's rule regarding the order of a reaction is inadmissible for heterogeneous systems, and so likewise is its application to reactions involving solid or colloidal catalysts.

In connection with Nernst's theory, a paper by A. Hantzsch on the absorption of ammonia gas by acids may be consulted.[2]

[1] *Zeit. physikal. Chem.*, 1904, **47**, 56. [2] *Ibid.*, **48**, 289.

Electrolytic Conductivity at High Temperatures.

The first part of an investigation of the electrical conductivity of aqueous solutions at high temperatures has been published by A. A. Noyes and W. D. Coolidge.[1] The substances chosen were sodium and potassium chlorides, and the range of temperature extended to 306°, the vessel used being a platinum-lined bomb. The range of concentration was from decinormal to 0·0005-normal. It was found that the molecular conductivity at infinite dilution, and therefore the ionic velocity is approximately a linear function of the temperature. The ratio $\frac{\mu_\infty \text{ KCl}}{\mu_\infty \text{ NaCl}}$ diminishes from 1·19 at 18° to 1·04 at 306°. The degrees of dissociation of the two salts are nearly identical at all temperatures. In decinormal solutions, the degrees of dissociation are approximately as follows:

18°.	140°.	218°.	281°.	306°.
0·84	0·79	0·74	0·67	0·60

The change is accurately expressed by the formula $(1-x)/\sqrt{c} =$ constant.

"Insoluble" Salts.

W. Böttger[2] gives the results of an investigation into the solubility of "insoluble" salts of silver, lead, and thallium. In all, about thirty substances were investigated. F. Kohlrausch also gives a useful table of the solubilities of a similar number of sparingly soluble substances, the values being deduced from his own conductivity data.[3]

Conductivity in Non-aqueous Solvents.

A great deal of experimental work has of late years been done on the properties of conducting solutions with non-aqueous solvents. As yet very few general points of view have been gained, the most important being that a certain affinity between solvent and solute is necessary in order that conduction, that is, ionisation, may take place at all.[4] The regularities observed in aqueous solutions are mostly absent, and very frequently the molecular conductivity of the dissolved substances is found to diminish with dilution instead of increasing as it does in aqueous solutions. In many cases, a maximum molecular conductivity is noted. The chief workers in this field at present are

[1] *Zeit. physikal. Chem.*, 1904, **46**, 323. [2] *Ibid.*, 521.

[3] *Ibid.*, **50**, 355.

[4] J. W. Walker, *Trans.*, 1904, **85**, 1082. Steele, McIntosh, and Archibald, *Proc. Roy. Soc.* 1905, **74**, 325.

Kahlenberg and his pupils, Walden, and recently Archibald, McIntosh, and Steele. Kahlenberg has devoted his energies chiefly to the accumulation of facts considered to be in opposition to Arrhenius's theory of electrolytic dissociation (which was evolved in the first instance for aqueous solutions only), and has discovered many interesting relations.[1] Walden, and still more Steele and his collaborators, are systematically accumulating data which may permit of the establishment of a general theory, possibly an appropriate modification of the theory of electrolytic dissociation. McIntosh, Steele, and Archibald, for example, have examined the liquefied hydrides of phosphorus, sulphur, and the halogens with respect to their vapour pressure, density, molecular surface energy, viscosity and its temperature-coefficient, the power of dissolving certain substances, the conducting power of the solutions thus obtained, the molecular weight of the dissolved substances, and the transport numbers, that is, the relative speeds of the ions produced.[2] From complete sets of data such as these it will no doubt soon become possible to determine in many cases what the ions are and the laws to which they are subject. Walden[3] gives a useful bibliography, chiefly for inorganic solvents, up to the end of 1902, and has supplemented this for organic solvents in the same journal (vol. **46**, 103). In the first of his papers, the experimental work is chiefly concerned with liquid sulphur dioxide as solvent; in the second, ammonium iodide is taken as a standard electrolyte, and the properties of its solutions in a great variety of organic solvents are investigated, as well as the necessary properties (conductivity, dielectric constant) of the pure solvents themselves.

H. C. Jones and C. G. Carroll,[4] and H. C. Jones and H. P. Bassett[5] have determined for solutions of various salts in mixtures of water with methyl and with ethyl alcohol the viscosity, the conductivity, and, for silver nitrate, the relative speeds of the ions at 0° and at 25°. In some mixtures of water and the alcohols, the dissolved salts exhibit a minimum conductivity, which is traced by the authors to a minimum of fluidity shown by the mixed solvent. In certain mixtures, notably 50 per cent. methyl alcohol, the degree of ionisation of certain salts is greater than that in pure water. The authors propose as a hypothesis: The conductivities of comparable equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, acetone, &c.) are inversely proportional to the coefficient of viscosity of the solvent and directly proportional to its

[1] Compare *Trans. Faraday Soc.*, 1905, **1**, 42, for a summary of his work and views.

[2] *Proc. Roy. Soc.*, 1904, **73**, 450; 1905, **74**, 320.

[3] *Zeit. physikal. Chem.*, 1903, **43**, 385.

[4] *Amer. Chem. J.*, 1904, **32**, 521.

[5] *Ibid.*, 409.

association factor as determined by the method of Ramsay and Shields. From a comparison of the conductivities at 0° and at 25°, the influence of one component of the solvent on the other apparently diminishes with rise of temperature. The relative velocities of the anion and cation of silver nitrate are largely dependent on the composition of the solvent and on the temperature.

Hydration of Ions.

The question of the hydration of ions in aqueous solution has of late received a considerable share of attention, and is a special case of the larger question of the combination of solute with solvent. From a consideration of the effect of temperature on the conductivity and fluidity of aqueous electrolytic solutions and of pure water, Kohlrausch[1] presents the hypothesis that about every ion, and moving along with it, there is an atmosphere of the solvent whose dimensions are determined by the individual characteristics of the ion, and that the electrolytic resistance of an ion is a frictional resistance which increases with the extension of the atmosphere, the direct action between the ion and the outer portion of the solvent diminishing as the atmosphere becomes of greater thickness. This hypothesis is in agreement with the fact that the most sluggish ions have a temperature-coefficient of resistance very like the temperature-coefficient of the viscosity of water, for the most sluggish ions would be those which move surrounded by the largest atmosphere of water, and the resistance they would experience would be practically that of water against water, and thus would be of the same nature as the viscosity of pure water. The hypothesis is further in agreement with the circumstance that the temperature formula for the mobility of the ions shows in all cases a convergence towards a zero value between $-35°$ and $-41°$, the zero value of the fluidity of water being reached at about $-34°$.

P. Vaillant[2] has investigated the density of aqueous solutions of electrolytes as composed additively of moduli dependent on the positive and negative ions. He concludes that the modulus of a given ion for any particular salt solution diverges from the mean value the more the salt is hydrated. The ions he considers to be mostly non-hydrated, with exceptions in the case of hydroxides, fluorides, sulphides, and carbonates, the anions of which are monohydrates.

Lobry de Bruyn[3] has electrolysed a solution of silver nitrate dissolved in a mixture of water and methyl alcohol. If either ion is hydrated, water will move with the ion to the corresponding electrode,

[1] *Proc. Roy. Soc.*, 1903, **71**, 338.
[2] *Compt. rend.*, 1904, **138**, 1210.
[3] *Rec. trav. chim.*, 1904, **22**, 430.

and thus the proportions between water and methyl alcohol around the electrodes will vary as the electrolysis proceeds. Experiment shows no variation in the proportions of water and alcohol in either the anodic or cathodic compartment, whence it appears that both $Ag^{\cdot}$ and NO_3' are anhydrous in the solution investigated, unless indeed the water transported by the ions in opposite directions should have been exactly equal in amount.

J. L. R. Morgan and C. W. Kanolt, on the other hand, have found[1] that, in the electrolysis of a mixed solution of pyridine and silver nitrate in water, pyridine travels from the anode to the cathode, thus accompanying the silver ion. They adopt the assumption of the formation of complex ions with the solvent.

Divergence from Dilution Law.

The problem of the divergence of strong electrolytes from the law which is valid for feeble electrolytes (Ostwald's dilution law) still awaits a final answer. A critical analysis of the experimental data bearing on the point is given by A. A. Noyes (*Technological Quarterly*, 1904, **17**, 293), who favours the view that the ionisation is deducible with accuracy from the conductivity data, and that the law of mass action is not directly applicable to the equilibrium between ions and non-ionised salt. A possible disturbing influence is discussed by Abegg and Labendzinski,[2] namely, the formation of complex ions in salt solutions. Hittorf, as long ago as 1859, showed that a solution of cadmium chloride, besides the simple ions, now represented as $Cd^{\cdot\cdot}$ and $2Cl'$, must contain a considerable quantity of complex anions of a general formula $(CdCl_2)_n(Cl')_m$. Arrhenius confirmed this in 1888 from his comparison of freezing point depressions and ionisations deduced from the molecular conductivity. The authors have now for a large number of salt solutions determined the electrode potential of the metal which acts as cation in the solution, and from this by Nernst's theory have deduced approximate concentrations for the simple metallion in the solutions. The metallic radicles in the salts investigated were Zn, Cd, Fe, Co, Ni, Pb, Cu; the negative radicles were NO_3, Cl, SO_4, $C_2H_3O_2$. The concentrations deduced were in many cases much smaller than those which would be calculated from the conductivity, thus indicating the formation of complex ions containing the metal. For a given metal, the tendency to form complex ions depends greatly on the nature of the negative ion. The nitrates form almost exclusively simple ions; in the chlorides, sulphates, and acetates, the proportion of complex ion present

[1] *Zeit. physikal. Chem.*, 1904, **48**, 365.
[2] *Zeit. Elektrochem.*, 1904, **10**, 77.

increases in the order indicated. The effect of the addition of alkali salts with the same anion indicates that the complex ions are for the most part complex anions, as in the case of cadmium chloride alluded to above. In solutions of acetates rendered very rich in complex ions by the addition of alkali acetate, the concentration of the simple metallion increases as the solution is diluted owing to the breaking up of the complexes. It is evident that for such salts Ostwald's dilution law cannot apply, as in its ordinary application it is assumed that only simple ions exist in the solutions.

Amphoteric Electrolytes.

Another class of substances which do not obey Ostwald's dilution law except as a limiting case is to be found in amphoteric electrolytes, such as the aminobenzoic acids. These acids yield conducting solutions, and when the molecular conductivity is worked up in the ordinary way so as to determine the degree of ionisation, it is found that no constant is obtained when the simple Ostwald formula is applied, the value of the expression $\frac{m^2}{(1-m)v}$ falling to a minimum and then rising as dilution proceeds. This was attributed by Ostwald and Wislicenus to molecular association, the basic portion of one molecule neutralising the acid portion of another. This assumption has been shown to be unnecessary by J. Walker,[1] who has worked out the theory of amphoteric electrolytes on the basis of the theory of electrolytic dissociation. If the true acid constant k_a, the true basic constant k_b, the ionisation constant of water K, and the concentration of the non-ionised proportion be known, the concentrations of all the ions present may be calculated. The reason why Ostwald's dilution formula does not apply to such acids is that besides the positive hydrion $H^{\cdot}$ (alone assumed to be present in deducing the dilution formula) there is present another positive ion $HX^{\cdot}$ of different ionic velocity. The quantity of the ion $HX^{\cdot}$ is far from negligible, even when k_b is very small. Thus for *o*-aminobenzoic acid, with $k_a = 1{\cdot}04 \times 10^{-5}$ and $k_b = 1{\cdot}34 \times 10^{-12}$, the ratio of the concentration of $HX^{\cdot}$ to $H^{\cdot}$ at various dilutions is as under:

	v = 64.	128.	256.	512.	1024.
$(HX^{\cdot})/(H^{\cdot})$ ...	1·63	0·81	0·40	0·20	0·10

Knowing the concentrations of the various ions and their ionic velocities, the molecular conductivity of the solutions may be calculated. Close accordance between the theoretical and observed results has been found with the three aminobenzoic acids, cacodylic acid, and asparagine. The proper application of the theory of electrolytic dissocia-

[1] *Proc. Roy. Soc.*, 1904, **73**, 155, and **74**, 271.

tion has here explained away a class of apparent exceptions to the theory, the apparent divergence being due to an improper assumption regarding the nature of the ions present, just as is the case with the complex ions referred to in the preceding section.

Relative Strengths of Acids and Bases.

R. C. Farmer and F. J. Warth[1] have applied to the determination of the affinity constants of bases the method of distribution-ratios developed by the former for acids.[2] The bases investigated were all derivatives of aniline and the naphthylamines. The acid employed was hydrochloric acid, and the solvents were water and benzene. The method is in general of easy application, and gives satisfactory results for feeble bases.

C. Tubandt[3] has applied the inversion of *l*-menthone to the study of reaction velocity in absolute alcohol, and of the relative strengths of acids and bases in this solvent. The action, like the inversion of cane sugar in aqueous solutions, may be followed by means of the polarimeter. The rotation is proportional to the concentration, and the point of equilibrium is independent of the nature of the substances used to effect the inversion. Sodium ethoxide inverts the menthone at a rate proportional to its concentration when the concentration is high; in dilute ethoxide solutions, the effect is relatively greater. The presence of neutral salts and esters was found to have little or no influence on the rate of reaction. The addition of water or of benzene to the solvent reduced the velocity. Sodium hydroxide and the quaternary ammonium bases gave high inversion constants of the same order of magnitude. Powerful acids gave even higher constants than the bases, but the constant in the case of hydrochloric acid was not even approximately proportional to the concentration of the acid. Hydrochloric acid was found to invert the menthone in benzene solution. Weak acids, such as acetic acids and phenols, were practically without action in alcoholic solutions, and the amine bases were also inactive.

The method was applied to the investigation of the relative acidic strengths of esters, such as ethyl malonate and ethyl acetoacetate. These substances were in themselves too feebly acid to exert any inverting action in alcoholic solution. The method adopted therefore was analogous to that by means of which the relative strengths of feeble acids in aqueous solution may be determined by the hydrolytic dissociation of their salts. The sodium compounds of the esters when dissolved in water undergo "alcoholytic dissociation," and the amount

[1] *Trans.*, 1904, **85**, 1713. [2] *Ibid.*, 1901, **79**, 863.
[3] *Dissertation, Halle*, 1904.

of sodium ethoxide produced may be determined by the rate of inversion of the menthone. Ethyl acetoacetate was found to be much more strongly acid than ethyl malonate, the relative degrees of alcoholytic dissociation being respectively 6 and 68 per cent. in corresponding solutions. Disodium compounds are apparently not produced in measurable quantity. The replacement of a hydrogen atom in ethyl acetoacetate by an alkyl group results in a diminution of the acid character of the ester, the diminution being greater the larger the radicle.

With varying proportions of ester and sodium ethoxide, and with varying dilutions, it was found that the degree of alcoholysis was in accordance with the same law as regulates the degree of hydrolysis in aqueous solutions.

Ethyl cyanoacetate is approximately as strong an acid as ethyl acetoacetate; deoxybenzoin is weaker than ethyl malonate; acetylacetone is a comparatively strongly acid substance, and dimethyldihydroresorcin still stronger. Phenol is intermediate between ethyl malonate and ethyl acetoacetate. Acetanilide is neutral, acetoxime feebly acid, succinimide and phthalimide strongly acid. Dimethylpyrone is neutral and hydrocyanic acid somewhat more feeble than ethyl acetoacetate.

The method is of special importance as affording a means, hitherto wanting, of investigating the acidic and basic character of substances in alcoholic solution, and also as affording information as to the ionising nature of the solvent itself.

Pseudo-acids and Pseudo-bases.

According to Hantzsch, pseudo-acids and pseudo-bases are characterised, amongst other properties, by the hydrolysis of their salts in aqueous solution having an abnormal value. This relation seems to be proved experimentally in a great number of cases. It does not, however, accord with Hantzsch's conception of the nature of the relation between acid and pseudo-acid, which may be expressed briefly by the equilibrium equation

$$\text{Acid} \rightleftarrows \text{Pseudo-acid},$$

or one that may be derived directly from this. Hantzsch's theory, as far as salt-hydrolysis is concerned, is based on the theory of electrolytic dissociation; but, as H. Kauffmann[1] has shown, a consistent application of the dissociation theory to the problem leads to the conclusion that the hydrolysis of the salts of the pseudo-acid should be normal. Hantzsch's theory of pseudo-acids and pseudo-bases cannot therefore be accepted as it stands. J. v. Zawidzki has

[1] *Zeit. physikal. Chem.*, 1904, **47**, 618.

assumed that the abnormal behaviour of pseudo-acids is accounted for by the assumption that they are amphoteric electrolytes. The dissociation theory of amphoteric electrolytes, however,[1] does not admit of the validity of this assumption as a general solution of the problem, although it might in some cases account for abnormal hydrolysis.

Indicators.

Several interesting papers on the indicators of acidimetry and alkalimetry have been published by Friedenthal, Salessky, Fels, and Salm.[2] Friedenthal proceeds in a systematic way to classify acid or alkaline solutions according to the concentration of hydrion existing in them. The concentrations are expressed in terms of a normal solution of hydrion, the boundaries between successive grades in the classification being the successive powers of 10. Judging from Kohlrausch's conductivity data, the solution of maximum concentration of hydrion is 5·8-*N* nitric acid, in which hydrion is approximately 2-*N*. The solution of minimum concentration of hydrion is about 6·7-*N* potassium hydroxide, which is about 2-*N* hydroxidion or 5×10^{-15}-*N* hydrion at 24°. In the present writer's opinion, it is inadvisable to carry the classification by means of hydrion into the region beyond neutrality, since the product hydrion × hydroxidion, whilst constant for any one temperature, varies greatly with changing temperature, and therefore hydrion concentrations derived by calculation from known hydroxidion concentrations are liable to great fluctuations with temperature, although the hydroxidion concentrations may themselves remain practically constant. It would seem therefore that the grade of an alkaline solution would be most appropriately expressed, for the more concentrated solutions at least, by a concentration of hydroxidion instead of a concentration of hydrion. The figures given by Friedenthal are only applicable at 24°, when hydrion × hydroxidion $= 10^{-14}$.

In the regions more concentrated than millinormal hydrion (hydrochloric acid) on the one hand, and millinormal hydroxidion (potassium hydroxide) on the other, there is no practical difficulty in defining the grade of acidity or alkalinity. There are seven grades between these solutions, however, forming the region of "neutrality," the absolutely neutral solution being that in which hydrion = hydroxidion $= 10^{-7}$ at 24°.

According to the indicator employed, the point of "neutrality" may be indicated in any of these grades, but the best indicator for absolute

[1] Walker, *ante*, p. 19.

[2] *Zeit. Elektrochem.*, 1904, **10**, Friedenthal, p. 113 Salessky, p. 204, Fels, p. 208, Salm, p. 341.

neutrality will be that which indicates hydrion at a concentration as little as possible greater than 10^{-7}, and similarly hydroxidion at a concentration as little as possible greater than the same value. Of the ordinary indicators, methyl-orange changes between 10^{-4} H· and 10^{-5} H·, *p*-nitrophenol between 10^{-5} H· and 10^{-6} H·, and phenolphthalein between 10^{-5} OH′ and 10^{-6} OH′. Litmus, when pure, indicates on the one hand 10^{-6} H· and on the other 10^{-6} OH′; lacmoid is somewhat similar. Litmus would therefore seem to be the best indicator for indicating actual proximity to the neutral point. Friedenthal suggests the preparation of solutions of any required very small concentration of hydrion or of hydroxidion by the mixing of NaH_2PO_4 and Na_2HPO_4 in various proportions. This method has been tested by Salm by means of *E.M.F.* measurements with hydrogen electrodes, and is found to be satisfactory. Salm gives a very complete table of indicators (27 in number) with regard to their behaviour at the various grades of concentration of hydrion and hydroxidion. By means of these indicators, it should be possible to estimate the grade of acidity, neutrality, or alkalinity of any given aqueous solution. Scholtz in a supplementary paper [1] discusses the behaviour of mixtures of these indicators.

Catalysis.

M. Bodenstein,[2] in an investigation of the catalytic effect of platinum in promoting the combination of oxygen and hydrogen, has observed that in presence of compact platinum the action takes place at the ordinary temperature with measurable velocity.

P. V. Bevan,[3] in a paper on the combination of hydrogen with chlorine in presence of light, has detected the formation of an intermediate substance which can act as a cloud nucleus before any hydrogen chloride is produced. The most probable assumption in his opinion is that chlorine first combines with traces of water vapour, the compound produced then reacting with hydrogen to form hydrochloric acid with regeneration of water.

Bredig and Stern [4] have investigated the nature of the catalytic action effected by potassium cyanide in the benzoin reaction. They found that the reaction is of the second order with regard to benzaldehyde and that the velocity constant of the reaction is directly proportional to the concentration of the potassium cyanide present. Sodium cyanide and barium cyanide have the same accelerating action as potassium cyanide. The authors conclude that the catalytic action is

[1] *Zeit. Elektrochem.*, 1904, **10**, 549.
[2] *Zeit. physikal. Chem.*, 1904, **46**, 725.
[3] *Phil. Trans.*, 1904, **202** A, 71.
[4] *Zeit. Elektrochem.*, 1904, **10**, 582.

due to cyanidion CN′, since the addition of any reagent, such as AgCN, which partially destroys cyanidion by formation of a complex ion, or otherwise, diminishes the velocity. This conclusion is in accordance with the fact that hydrocyanic acid and mercuric cyanide exert no appreciable effect in the benzoin synthesis, these substances being practically non-ionised. Alkali alone does not promote the formation of benzoin, and when added to potassium cyanide diminishes the velocity constant due to the latter. The authors conceive the simplest explanation of the mechanism of the action to be as follows:

(1) $C_6H_5 \cdot COH + CN' = C_6H_5 \cdot CH(CN) \cdot O'$;
Anion of mandelic nitrile.

(2) $C_6H_5 \cdot CH(CN) \cdot O' + C_6H_5 \cdot COH = C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5 + CN'$.

Enzyme Action and Sugar Inversion.

The part played by enzymes and by acids in the inversion of sugars has been investigated by E. F. Armstrong and collaborators.[1] From a study of the results obtained, the authors conclude with Arrhenius that only a small proportion of the sugar is active at any one time, and this part they conceive to be in a state of combination with the enzyme or with the acid. They suppose that when an acid is added to a sugar solution there is competition for the acid by the sugar and by the water, so that the velocity of the inversion may vary in a somewhat complicated way with the proportions of sugar, acid, and water present. With small concentrations of acid in comparison with the sugar, the sugar-concentration seems at first to diminish as a linear function of the time, afterwards to become the logarithmic function characteristic of unimolecular reactions.

In the above conception, the sugar acts, by reversible combination with the acid, as a base. The same idea in a somewhat different form is advanced by H. Euler,[2] who assumes that the active sugar is the cathion $C_{12}H_{21}O_{10}^{\cdot}$, the sugar being ionised as a base into this cathion and OH′. When HCl is added to the sugar solution, the salt $C_{12}H_{21}O_{10}{}^{\cdot}Cl'$ will undergo the ordinary hydrolytic dissociation exhibited by salts of weak bases. In dilute solutions, the concentration of the salt will be proportional to the concentration of the acid.

J. W. Mellor and L. Bradshaw[3] give a theoretical discussion of the velocity of sugar inversion on the assumption that it is primarily a unimolecular reaction followed by two subsidiary unimolecular reactions, the subsidiary actions which they have in view being the conversion of dextrose and lævulose into the birotatory forms. This

[1] *Proc. Roy. Soc.*, 1904, **73**, 500 *et seq.* ; **74**, 188 *et seq.*
[2] *Zeit. physikal. Chem.*, 1901, **36**, 644 ; 1904, **47**, 353.
[3] *Ibid.*, 1904, **48**, 353.

assumption accounts for the simple unimolecular constant attaining a maximum with time and then diminishing. A numerical example calculated by the authors shows a satisfactory agreement with experimental values.

H. P. Barendrecht[1] advances a hypothesis to account for the action of invertase on sugar showing a departure from the normal logarithmic law for unimolecular reactions, and for the retarding influence exerted on the reaction by the addition of dextrose, lævulose, mannose, galactose, &c. He assumes that the enzyme exerts its specific action by radiation. In the case of cane sugar, this radiation is stopped by the cane sugar itself, and also to some extent by the products of its inversion, and by foreign sugars such as galactose, whence their retarding influence. So long as the cane sugar is of sufficient concentration to absorb all the radiation before it is reduced to such an extent as to be unable to cause inversion, one particle of the enzyme will in a given time invert the same amount of sugar, whatever the concentration of the sugar may be. When the concentration of sugar is below this limiting value, the amount of sugar inverted in a given time by a given amount of enzyme will depend on the concentration of the sugar, and at low concentrations will follow the unimolecular law. The author gives a mathematical formulation of his hypothesis, and applies it to the study of the inversion of cane sugar and of maltose, alone and in presence of other carbohydrates and of glucosides.

Time Conception of Minute Concentrations.

Bodländer and Eberlein[2] have recently determined from *E.M.F.* measurements the equilibrium-constant

$$\frac{[Ag^{\cdot}][CN']^3}{[Ag(CN)_3'']} = 1{\cdot}13 \times 10^{-22}.$$

From this it may be calculated that the concentration of argention $Ag^{\cdot}$ in normal solution of potassium-silver-cyanide is 8×10^{-24} equivalents per litre. Assuming the ordinary atomic dimension, that is, 10^{24} atoms in the gram atomic weight, this concentration would only give 8 atoms per litre, a result which can scarcely be reconciled with the ease with which metallic silver may be deposited electrolytically from such a solution. Ostwald, in order to avoid this difficulty, suggested that the equilibrium might be conceived in such a manner that every silver atom in the solution might be imagined to pass through the stage of the metallic ion, so that the very small apparent concentration would then indicate the ratio of the time of existence of any one silver atom as argention

[1] *Zeit. physikal. Chem.*, 1904, **49**, 456.
[2] *Zeit. anorg. Chem.*, 1904, **39**, 167.

to the time of its existence in the complex ion. F. Haber [1] has subjected this conception to a closer analysis and comes to the conclusion that the original difficulty still remains, although its form has changed. The above expression looked at from the new point of view becomes

$$\frac{\text{Time of formation of complex ion}}{\text{Time of decomposition of complex ion}} = 1{\cdot}13 \times 10^{-22}$$

for unit concentrations. Supposing now the numerator had the value 1/1000 or 1/10,000 sec., a normal solution of $Ag(CN)_3''$ would take thousands of years to yield an amount of $Ag^{\cdot}$ which could be detected. This, again, is in opposition to the ease of electro-deposition of silver from cyanide solution. If, on the other hand, we suppose that even in extremely dilute solutions argention is pretty rapidly produced, that is, if we make the denominator equal to about 10^{-2} sec., the numerator will become 10^{-24} sec. The formation or decomposition of the complex ions is, however, associated with the movement of electrical charges, and it is consequently difficult to conceive any reason why such an electrical change should occur at a greater rate than that which would be deduced from the velocity of propagation of electric disturbance, say the velocity of light. Now light would travel a distance equal to the average atomic dimensions in 10^{-18} seconds. But the above calculation shows that for the formation of the complex ion at unit concentration only one-millionth part of this time is required. The author concludes that the very small ionic concentrations calculated from *E.M.F.* measurements have probably no real existence, although their value in calculations remains unimpaired. From the point of view of the atomic theory, the author considers a concentration of 10^{-14} normal to be the smallest that can be accepted without question. Bodländer, Abegg, and Danneel [2] have subjected the author's views to criticism: he maintains, however, his position, and puts the matter in its wider application thus. When ionic concentrations are of ordinary dimensions, reactions take place for the most part between the ions. When, however, the ionic concentrations are excessively small, the concentrations of the non-ionised substances remaining great, then the bulk of the reaction will be between non-ionised substances, although the velocity-constant for them may be many times smaller than the velocity-constant for the ionic reaction, when both are referred to the same concentration. In short, he considers the ionic reactions to have velocity-constants some thousandfold greater than those for reactions of undissociated substances, the difference in favour of the former being due to the mobility of the electrons, and likens the relation between ions and non-ionised substances as regards their activity to

[1] *Zeit. Elektrochem.*, 1904, **10**, 433. [2] *Ibid.*, 604 *et seq.*

that which exists between the hydrogen compounds of organic radicles on the one hand and the corresponding alkyl compounds on the other. This statement of Haber's views may be compared with that of J. Wallace Walker[1] and with the results of Kahlenberg.[2]

Passivity of Metals.

Some general points regarding the passivity of metals are raised by O. Sackur.[3] Zinc fails to precipitate copper from solutions of the double cyanide or thiocyanate, nickel and cadmium from the nitrates, and iron from the sulphate. From the sulphates and chlorides of nickel and cadmium, on the other hand, and from the nitrates of lead and copper, the metals are at once precipitated by zinc. In the first set of instances, the zinc is passive, but the passivity may be removed to any desired degree by the gradual addition of chlorides or of free acid. The same gradual increase of activity has been shown by other observers for chromium, iron, and nickel. The passivity of zinc appears, therefore, to be conditioned by two factors: first by the absence of certain ions, and secondly by the approximation in the electrochemical series of zinc and the metal to be precipitated. The explanation of passivity is consequently to be sought in the domain of reaction velocities, as has already been suggested by Le Blanc. In favour of this view there is the increased activity with rise of temperature, and also the dependence of activity on current density in the case of anodic polarisation.

According to the Drude-Riecke theory of metallic conduction, the positive electrons are bound to matter, whilst the negative electrons are freely mobile. In a metal, then, the transport of electricity takes place entirely by the motion of negative electrons. In an electrolyte, both electrons move in association with matter. The author assumes that the mode of discharge of anions is essentially different from that of cathions. At the anode, the primary action is that the anion loses its negative charge, which passes off through the metal; no positive electron comes from the metal. At the cathode, on the other hand, there is actual neutralisation by negative electrons leaving the metal with consequent separation of the discharged cathion. In the case of a metal dissolving according to Faraday's law, the actions at the anode may be represented as follows:

$$SO_4'' = SO_4 + 2\ominus.$$
$$SO_4 + Cu = CuSO_4.$$
$$CuSO_4 = Cu'' + SO_4''.$$

[1] *Trans.*, 1904, **85**, 1082.
[2] *Zeit. physikal. Chem.*, 1904, **46**, 68.
[3] *Zeit. Elektrochem.*, 1904, **10**, 841.

The point in which this conception differs from Nernst's theory in its original form is that there is no primary formation of metallion from metal. Similarly, a complex compound would be formed from metal and discharged anion directly, so that Haber's difficulty regarding the very small ionic concentrations deduced from Nernst's theory in great measure disappears, as it becomes possible to regard them as fictitious magnitudes (compare p. 26).

When the anode is a noble metal and not attacked by the discharged anion, the free energy necessary for the continuous discharge of the anion must be supplied. This is also the case when the action between discharged anion and metallic anode is possible, but does not occur rapidly enough to depolarise all anions brought by the current. The metal is then passive, and may show any electrode potential between its own active value and that of a noble metal. The velocity of the anode reaction depends on the nature of the metal and of the discharged anion, passivity being of most frequent occurrence with anions capable of yielding oxygen. A protective coating of oxide may occasionally be the cause of the small velocity, but this must be proved for each case, and not assumed as a general explanation. The proof has been given for aluminium by Taylor and Inglis, and for iron in fused caustic soda by Haber and Bruner. Protective coatings of gas may also be reconciled with the author's hypothesis.

The oxidising anions, NO_3', ClO_3', &c., promote passivity to the greatest extent; Cl′ and Br′ practically exclude passivity; SO_4'', CN′, CNS′, $C_2H_3O_2'$, OH′, are intermediate. Of the cations, only one, $H^{\cdot}$, has any effect, and its action always tends against passivity. From a consideration of these facts, it may be concluded that, apart from complications by oxide-films, &c., the anodic solution of metals must be determined by the velocity of some action involving hydrogen. The author presents the following hypothesis as to the nature of this intermediate action. If M is a bivalent metallic electrode which does not decompose water (and only such are capable of becoming passive), then the action

$$M + 2H^{\cdot} \rightleftarrows M^{\cdot\cdot} + H_2,$$

which probably takes place very rapidly, can only proceed to a very small extent, namely, to the equilibrium concentration of H_2, if the discharged hydrogen is not at once removed. The removal may take place by combination with the discharged anion, the halide anions being particularly active in this respect, the oxygen anions slow. Increased acidity must displace the equilibrium towards the second member of the equation and thus promote solution; in this way the action of acid in reducing passivity is accounted for. The slowness of the combustion of hydrogen at the anode may be caused by (1) its small concentration,

for example, with the noble metals, or (2) by the deficient contact with the metallic electrode. If this second condition is the cause of passivity, it follows that those metals will tend to become passive which do not exercise a catalytic action on the union of hydrogen and oxygen, whilst those which exert such a catalytic action will have little tendency to become passive. The data for testing this relation between passivity and the behaviour of metals in the oxyhydrogen gas-cell are as yet rather meagre, but such data as exist are in favour of the hypothesis.

W. Muthmann and F. Frauenberger[1] find by Hittorf's method that molybdenum, vanadium, tungsten, niobium, and ruthenium may be made passive in normal potassium chloride solution. Uranium and manganese under the same conditions remain active. Passivity is brought about by exposure to oxidising agents, especially to oxygen acids, and is always greatest with anodic polarisation. Cathodic polarisation in acids, salts, or bases increases the activity of the metals. On exposure to air, the metals become passive, their potential assuming a value intermediate between the extremes. Thorough mechanical cleansing of the surface is almost as effective as cathodic polarisation in increasing the activity. Iron, nickel, and cobalt were investigated in normal solutions of their sulphates and exhibited the same phenomena. The maximum potentials found for these metals were several decivolts above those determined by Neumann, which were probably "air-potentials." The authors account for their results by assuming that oxygen from the air or from an oxidising agent is absorbed at the metallic surface with formation of a solid solution, so that the potential of the passive metal is that of a metal-oxygen alloy. Sackur, in discussing these results,[2] thinks they are better explained by the assumption of a protective gas film which prevents good contact between the metal and the discharged activating chloridion.

In connection with the hypothesis of passivity being due to small reaction-velocity, reference may be made to Nernst's theory of velocity in heterogeneous systems (p. 14), which refers the rate of chemical action to a velocity of diffusion.

JAMES WALKER.

[1] *Sitzungsber. math.-phys. Bayer. Akad. Wiss.*, 1904, **34**, 201.
[2] *Zeit. Elektrochem.*, 1904, **10**, 929.

INORGANIC CHEMISTRY.

Reviewing the past year naturally calls to mind the fact that during its course many have passed away whose energies have been directed to the advancement of our knowledge of the elements and their compounds, and who have busied themselves with establishing sound theoretical explanations of the facts of the science of chemistry. Notably amongst these stands the name of Alexander W. Williamson, whose death on May 8th, at the ripe age of eighty, ended the career of a man the history of whose services to science takes us back to those times when chemistry was striving for clear views of the fundamental conceptions of "atom" and "molecule." In this country, Williamson's influence for the benefit of science has not been confined to his writings and teaching alone, but is also to be seen in the services he performed in the administration of the affairs of societies concerned with the advancement of science. On July 23rd died C. A. Lobry de Bruyn, for a short period prior to his death Professor of Chemistry at the University at Amsterdam, whose investigations cover a wide field and represent all branches of chemistry, and to whom we are indebted for the isolation of pure hydroxylamine and of pure hydrazine.

Professor Clemens Winkler died on October 8th, at the age of sixty-six; for many years he was associated in various capacities with the School of Mines at Freiberg, and throughout his life remained a constant and devoted worker in the department of inorganic chemistry. Winkler did much to develop and simplify the methods of volumetric and gas analysis, and by his devices has made the latter capable of everyday application in technical work. His researches made clear the requirements for the successful manufacture of anhydrosulphuric acid.

The discovery of germanium will always be reckoned amongst the great achievements of Winkler; the properties of this element supplied the third confirmation of the prediction by Mendeléeff of the properties of the elements required to fill the spaces in the system of elements arranged in the order of their atomic weights, and such confirmation has undoubtedly influenced the minds of chemists in their acceptance of the Periodic Law. Mendeléeff has recently demonstrated the elas-

ticity of this system in his speculations on the composition of the ether, set forth in the work translated by G. Kamensky, entitled "An attempt towards a Chemical Conception of the ether."

To the groups in the periodic system, in the first place, Mendeléeff proposes to add a zero group in front of group I. In this zero group are placed those elements, helium, neon, argon, krypton, and xenon, with the isolation and properties of which the researches of Sir W. Ramsay and his pupils have made us familiar; a group of elements characterised by their chemical inactivity, for which, therefore, valence is reduced to zero, and further, substances whose molecules are monatomic. Helium belongs to the second series commencing with lithium and ending with fluorine, whilst the first series is represented only by hydrogen, a homologue of lithium, that is, belonging to the same group. The element in the first series of the zero group is represented by "*y*," a substance which must have the properties characteristic of the argon gases. It is calculated from the relation of the atomic weights of the elements in the neighbouring group that this element has an atomic weight of less than 0·4. The relative density of "*y*" in relation to hydrogen would be 0·2, and it may be identified with the substance "coronium," whose spectrum was first observed by Young and Harkness in the corona during the eclipse of 1869. Nasini, Anderlini, and Salvadori considered that they had found traces of coronium in their examination of the spectra of volcanic gases (1893).

The molecules of "*y*" would not be sufficiently light, nor would their velocity be great enough, to identify this element with ether. To complete the series of elements, therefore, a zero series is added, and in this series in the zero group is placed an element "*x*," which Mendeléeff regards "(1) as the lightest of all the elements, both in density and atomic weight; (2) as the most mobile gas; (3) as the element least prone to enter into combination with other atoms, and (4) as an all permeating and penetrating substance." This element "*x*," it is suggested, is the ether, the particles and atoms of which are "capable of moving freely everywhere throughout the universe, and have an atomic weight nearly one-millionth that of hydrogen, and travel with a velocity of about 2,250 kilometres per second."

As Mendeléeff points out, "the conception of the ether originates exclusively from the study of phenomena and the need of reducing them to simpler conceptions. Amongst such conceptions we held for a long time the conception of imponderable substances (such as phlogiston, luminous matter, the substance of the positive and negative electricity, heat, &c.), but gradually this has disappeared, and now we can say with certainty that the luminiferous ether, if it be real, is ponderable, although it cannot be weighed, just as air cannot be

weighed in air, or water in water. We cannot exclude the ether from any space; it is everywhere and penetrates everything, owing to its extreme lightness and the rapidity of motion of its molecules. Therefore such conceptions as that of the ether remain abstract, or conceptions of the intellect, like the one which also leads us to the very teaching about a limited number of chemical elements out of which all substances in nature are composed."

The future will decide whether these ideas are destined to take a place among the accepted interpretations of natural phenomena; but the history of the reception of the first suggestions from which the "periodic law" has grown warns us against too dogmatic an attitude.

The record of the work in inorganic chemistry during the year 1904 gives evidence of great activity on the part of those chemists who cultivate this special department of research; whilst, possibly, the discoveries may be lacking in the sensational nature of those which have characterised the two previous years, still there is a rich store of material, containing much that gives precision to our knowledge of elements and compounds where such exact information has been wanting. The very nature of this material and its varied character, which of necessity arises from the number of the elements and their numerous compounds, makes the writing of a Report of this kind a matter of considerable difficulty, and necessitates the selection of researches which can be dealt with from a few general points of view.

Thus, for example, we may take in the first place some of the results which have accrued from the investigations carried out under conditions which the ready command of low temperatures has made possible. The study of the compounds formed by liquid halogen hydrides and organic substances, such as acetone and ether, by Archibald and McIntosh,[1] offers an instance of this kind. The composition of these compounds is shown to find a simple explanation in the increased valency of oxygen at low temperatures. Thus the compound $(C_2H_5)_2O,HI$, it is suggested, may be regarded as containing a quadrivalent oxygen atom, thus: $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}H\\I\end{matrix}$, rather than a simple additive compound; similarly, $(CH_3)_2CO,HBr$ is represented as $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!:\!O\!<\!\!\begin{matrix}H\\Br\end{matrix}$. Whilst these and other similar substances indicate the influence of temperature on the valence of oxygen, the further investigations of such substances may realise in compounds such as $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}H\\Br\end{matrix}$, and $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}SnCl_3\\Cl\end{matrix}$ the asymmetry of the oxygen atom.

[1] *Trans.*, 1904, **85**, 919.

Stock and Guttmann,[1] in their researches on antimony hydride, have availed themselves of liquid air to liquefy and solidify this gas, which is best prepared by the action of hydrochloric acid upon an alloy of magnesium and antimony containing 33 per cent. of the last-named metal. Exact determinations of the physical constants of this compound have been made, its solubility in many solvents noted: whilst it is readily soluble in ether, ligroin, and benzene, these solutions quickly become turbid; carbon disulphide is essentially the solvent for this gas, dissolving 250 times its own volume. It is readily decomposed by electric discharge, and at times decomposes spontaneously into antimony and hydrogen. The dry gas is stable, the presence of moisture promotes its instability, and it is attacked by the air at the ordinary temperature. It reacts readily with oxygen forming antimony and water, and converts nitric oxide into nitrous oxide, nitrogen, and ammonia, antimony being formed at the same time. The halogens decompose it readily. By the action of air or oxygen on the liquid at $-90°$, an unstable yellow modification of antimony is formed, which dissolves in carbon disulphide, forming an intensely yellow solution. At $-50°$, this form passes into the metallic variety of antimony.

By vaporising arsenic in a vacuum and condensing the vapours by liquid air, the quantitative conversion into yellow arsenic has been effected by Stock and Siebert.[2]

Francesconi and Sciacca[3] have studied the interaction of liquid nitric oxide and liquid oxygen, obtaining in this way nitrogen trioxide, which is also formed by gaseous nitric oxide and oxygen at $-110°$; the conversion of nitrogen peroxide into nitrogen trioxide by nitric oxide takes place at $-150°$. The trioxide is stable under the ordinary pressure at $-21°$. Wittorf,[4] in the investigation of the melting points of mixtures of nitrogen peroxide and nitric oxide, obtained a blue liquid of the composition N_2O_3, which solidifies to a blue solid melting at $-103°$; with increase in proportion of nitrogen peroxide, the melting point falls to the eutectic point of $-112°$.

By treating sulphur chloride with liquid chlorine in sealed tubes, Ruff[5] has shown sulphur tetrachloride to be formed as a solid melting between $-30{\cdot}5°$ and $-31°$; the liquid formed readily decomposes—in fact, a few degrees above the melting point its dissociation pressure exceeds one atmosphere. A number of compounds of sulphur tetrachloride and chlorides of other elements are described, as also a compound with arsenic fluoride.

[1] *Ber.*, 1904, **37**, 885.
[2] *Ibid.*, 4572.
[3] *Gazzetta*, 1904, **34**, [i], 447.
[4] *Zeit. anorg. Chem.*, 1904, **41**, 85.
[5] *Ber.*, 1904, **37**, 4513.

From the cryoscopic study of the solution of chlorine in arsenic trichloride, Smith and Hora [1] conclude that the pentachloride is not formed as previously stated by Baskerville and Bennett.

Amongst other facts brought to light in researches at low temperatures are the demonstration of the fact that solid hydrogen is a crystalline and not a viscous solid,[2] the absorption of nitrogen by liquid oxygen described by Erdmann,[3] and the selective absorption for oxygen possessed by charcoal at very low temperatures affording, as Dewar [4] shows, a means of separating oxygen from nitrogen. Utilising the absorption of hydrogen by charcoal in vessels cooled by liquid hydrogen, Dewar has obtained vacua of so high an order that an electric discharge does not take place in the tube. From experiments made with helium in the same way cooled to 15° on the absolute scale, a vacuum is obtained in which the electric discharge produced only an intermittent phosphorescence; from his experiments, Dewar concludes that helium boils at about 6° absolute.

To Dewar [5] we are indebted for the determination of the densities of solid oxygen, nitrogen, and hydrogen, from which the molecular volumes of these elements at absolute zero have been calculated to be 21·21, 25·49, and 24·18 respectively. The latent heat of vaporisation of liquid oxygen and liquid nitrogen has been ascertained by Alt.[6]

Many instances of the application of electricity in the isolation of elements are recorded; especially noteworthy is the manufacture of metallic calcium by the electrolysis of fused calcium chloride, the device adopted by Messrs. Suter and Redlich, of Bitterfeld, obviating many of the difficulties surrounding this mode of producing the element. An iron cathode, so arranged that it can be slowly raised, dips on to the surface of the molten chloride, and when the metal has been formed round the end of the rod it is slightly withdrawn, so whilst still maintaining connection gives rise to the gradual production of a rod of the metal calcium. Some of the more important physical constants of this metal, purified by distillation, have been ascertained by Arndt,[7] who notes the energetic action of the metal on air, yielding calcium oxide and nitride (Ca_3N_2).

The electrolytic decomposition of solid caustic soda at temperatures near its fusing point is recorded by Haber and Tolloczko,[8] who also have similarly decomposed barium chloride at about 400° below its

[1] *J. Amer. Chem. Soc.*, 1904, **26**, 632.
[2] Travers (*Proc. Roy. Soc.*, 1904, **73**, 181).
[3] (*Ber.*, 1904, **37**, 1193); Erdmann and Bedford (*Ber.*, 1904, **37**, 1184).
[4] *Compt. rend.*, 1904, **139**, 261 and 421.
[5] *Proc. Roy. Soc.*, 1904, **73**, 251.
[6] *Ann. Physik*, 1904, [iv], **13**, 1010.
[7] *Ber.*, 1904, **37**, 4753.
[8] *Zeit. anorg Chem.*, 1904, **41**, 407.

melting point, and have noted that when barium carbonate is added to the chloride, carbon is observed to separate at the cathode. Further, when barium chloride is electrolysed in a current of carbon dioxide and air, the following reaction takes place:

$$BaCl_2 + CO_2 + O = BaCO_3 + Cl_2.$$

Calcium and sodium chlorides are each decomposed in a similar manner.

Coehn and Kettembeil[1] have found it possible to separate, in the form of an amalgam, barium from strontium, barium from calcium, and strontium from calcium by electrolysing solutions of the mixed chlorides, using a mercury cathode and varying potentials.

Coehn[2] shows that whilst radium is not deposited from solutions of its compounds in alcohol, acetone, or pyridine on a platinum cathode, it is deposited from its aqueous solutions on a mercury cathode, and this, when treated with hydrobromic acid, gives a permanently active bromide. Whereas the electrolytic separation of the alkaline earths is possible by using mercury cathodes, it is not possible to separate radium from barium save by working with currents of extremely low current density. Metallic radium is precipitated from its salt solutions by barium amalgam. In this connection, mention should also be made of Marckwald's[3] proposal to separate radium by treating solutions of radium barium chlorides with sodium amalgam.

Muthmann and Weiss have obtained the metals of the cerium group[4] by the electrolysis of the anhydrous chlorides, in some instances alone, in others by admixture with barium chloride. The metals were purified by fusion in crucibles made of pure magnesia, and covered with a layer of barium chloride; the action of lanthanum, neodymium, and praseodymium on silicates excludes the use of ordinary crucibles. Samarium is not readily obtained from its fused chloride, but has been produced by the electrolysis of a mixture of the chloride and barium chloride. In each case the cathode consisted of a small rod of carbon, and the current employed varied from 50—100 amperes. In the case of samarium, a layer of carbide is formed round the cathode, on which the metal is subsequently deposited. The metals have been obtained in quantities sufficient to establish definitely their physical appearance and constants, such as the specific gravities and their melting points. The latter constants were ascertained by heating the metals in magnesia crucibles under a layer of potassium and sodium chlorides, the liquefaction being indicated by the movement of a weighted rod of magnesia resting on the surface of the metal, the values found for the specific gravities being as follows: cerium, 7·0424; lanthanum,

[1] *Zeit. anorg. Chem.*, 1904, **38**, 198.
[2] *Ber.*, 1904, **37**, 811.
[3] *Ibid.*, 88.
[4] *Annalen*, 1904, **331**, 1.

6·1545; neodymium, 6·9563; praseodymium, 6·4754; samarium, 7·7—7·8; whilst the melting points were found to be for cerium 623°, lanthanum 810°, neodymium 840°, and praseodymium 940°.

These metals can all be burnt in the air, and the heats of combustion have been determined, giving in each case high values. The specific gravities afford an opportunity of deciding the position to which these elements may be assigned in the curve of atomic volumes and atomic weights, and support Benedick's[1] suggestion that these rare earths should occupy a position on the descending curve between barium and tantalum.

Alloys of cerium with aluminium, with magnesium, and with zinc, as also an alloy of lanthanum and aluminium, have been prepared by Muthmann and Beck.[2] These alloys combine with hydrogen at 200—400°, forming hydrides of cerium and lanthanum. The cerium magnesium alloy at 900° reacts with nitrogen forming the nitrides of these elements. Cerium forms a liquid, and also a solid amalgam with mercury, both of which readily decompose water with the evolution of hydrogen. Neodymium hydride, $NdH_2(?)_1$, and praseodymium hydride, $PrH_3(?)$, as also the nitrides NdN and PrN, have been formed by the direct union of the elements.[3]

By utilising the isomorphism of the double salt, bismuth magnesium nitrate with the corresponding double salts of magnesium nitrate and nitrates of the rare earths, Urbain and Lacombe[4] have succeeded in isolating a pure europium sulphate, the amount obtained representing 2 parts per 100,000 parts of monazite sand. It is a rose-coloured crystalline solid, having the composition $Eu_2(SO_4)_3,8H_2O$, and yields the oxide as a rose-coloured powder; the atomic weight assigned to the element is 151·79. These authors have also obtained pure samarium oxide, and give to this element the atomic weight 150·34.[5]

Nitrobenzene-*m*-sulphonic acid has been found by Holmberg[6] to form salts with neodymium, praseodymium, and lanthanum, the fractional crystallisation of which permits of the production of pure neodymium compounds.

R. J. Meyer[7] describes a series of complex double carbonates of the cerium earths and of the alkali metals; the potassium cerium carbonate has the composition $K_2Ce_2(CO_3)_4,12H_2O$, which may be taken as a type; these potassium compounds are readily soluble in aqueous solutions of potassium carbonate, and are precipitated from this solution on adding water in the following order: lanthanum, praseodymium, cerium, and neodymium. By the aid of these compounds, lanthanum can be completely separated from cerium and didymium.

[1] *Zeit. anorg. Chem.*, 1904, **39**, 41. [2] *Annalen*, 1904, **331**, 46.
[3] *Ibid.*, 58. [4] *Compt. rend.*, 1904, **138**, 84. [5] *Ibid.*, 1166.
[6] *Bihang. K. Svenska. Vet.-Akad.-Handl.*, 1902—1903, **28**, ii, No. 5, 7.
[7] *Zeit. anorg. Chem.*, 1904, **41**, 97.

That neodymium can be freed from lanthanum by the fractional precipitation of the chlorides by hydrogen chloride has been proved by Baskerville and Stevenson,[1] who also satisfied themselves of the unity of the neodymium chloride so purified. Baskerville's[2] attempts to prepare alums from the sulphates of lanthanum, praseodymium, and neodymium with those of rubidium and cerium have, while failing to yield alums resulted in the isolation of several double salts. By the action of concentrated sulphuric acid on cerium dioxide, the compound $Ce(SO_4)_2$, containing quadrivalent cerium, is formed,[3] which, if overheated, or if water is present in the sulphuric acid, decomposes with the evolution of oxygen and of ozone and the production of the cerosoceric sulphate, $HCe^{III}Ce^{IV}(SO_4)_4,13H_2O$. The stability and solubility relations of the hydrates of ceric sulphates have been examined by Koppel[4] with results differing from those of previous observers. The subject of the sulphates of the rare earths is dealt with by Brauner in two papers,[5] in one of which the production of complex sulphuric acids of the formula $M(SO_4H)_3$, in which M represents either cerium, lanthanum, praseodymium, neodymium, or samarium, is described. These compounds are formed by addition of concentrated sulphuric acid to a solution of the normal sulphate in ice-cold water; under similar conditions, thorium forms the salt $ThH_2(SO_4)_3$. Later, Brauner describes a series of salts of the complex cerisulphuric acid, such as $[Ce_2^{IV}(SO_4)_4]_3,Ce^{III}+44H_2O$, in which tervalent cerium may be replaced by lanthanum, praseodymium, and neodymium; these compounds are isomorphous with one another, forming mixed crystals.

A volumetric method for the ready determination of the atomic weights of the elements of the didymium and yttrium groups has been devised by Wild[6] which should materially facilitate the identification of the oxides obtained in separating these rare earths.

Cerium sulphide (Ce_2S_3) formed by the action of gaseous hydrogen sulphide on the oxide, hydroxide, sulphate, or carbonate at a red heat is not spontaneously inflammable,[7] whereas the oxy-sulphide prepared by the action of moist sulphuretted hydrogen is. Mosander's golden-yellow sulphide is shown to be crystallised ferric sulphide.

For the purpose of separating thorium from cerium, lanthanum, and didymium, *m*-nitrobenzoic acid has been advantageously employed by Neish,[8] the thorium salt, $Th(NO_2{\cdot}C_6H_4{\cdot}CO_2)_4$, being precipitated quantitatively from solutions of the nitrate.

When thorium oxide mixed with charcoal is heated in a tube of

[1] *J. Amer. Chem. Soc.*, 1904, **26**, 54.
[2] *Ibid.*, 64.
[3] Meyer & Autrecht, *Ber.*, 1904, **37**, 140.
[4] *Ibid.*, **41**, 377.
[5] *Zeit. anorg. Chem.*, 1904, **38**, 322, and **39**, 261.
[6] *Ibid.*, **38**, 191.
[7] Sterba, *Ann. Chim. Phys.*, 1904, [viii], **2**, 193.
[8] *J. Amer. Chem. Soc.*, 1904, **26**, 780.

silica in a stream of chlorine and the product separated by difference in volatility of the chlorides into three parts, the first fraction, according to Baskerville,[1] contains the chloride of *berzelium*, having an atomic weight 212, and of which the oxide is slightly radioactive. The second fraction contains the thorium chloride, whilst the third fraction is the chloride of a metal having the atomic weight 255·6 and styled *carolinium*. The ultra-violet spectrum between λ3444 and λ4071 exhibits, according to Sir W. Crookes, lines identical with those of thorium.

Turning to other rare elements, we find that by heating potassium zirconium fluoride with aluminium in an electric arc furnace, Wedekind[2] has obtained compounds of this metal and aluminium, and by substituting magnesium for aluminium the production of a crystalline substance containing 94·8 per cent. of zirconium takes place. The electrolysis of the fused potassium zirconium fluoride yields amorphous zirconium. The tetraiodide of zirconium (ZrI_4)[3] is produced when hydrogen iodide reacts on heated zirconium or its carbide; the sublimate is purified by treatment with benzene. It is a yellow, microcrystalline solid, which fumes in the air, is attacked vigorously by water, reacts with alcohol forming ethyl iodide and zirconic acid, and forms additive compounds with ether, ammonia, and propylamine. The oxy-iodide, $ZrOI_2,8H_2O$, corresponding to the oxychloride and oxybromide, is formed by action of water on the iodide or by action of hydriodic acid on zirconium hydroxide, $Zr(OH)_4$ (Stühb and Denk).

Indium and its compounds have been the subject of investigation by several chemists. Thiel[4] gives from the analyses of the chloride a value for the atomic weight of 115·08 ± 0·03, whilst from the bromide the value 114·81 ± 0·07 is deduced; the metal has been obtained by the electrolysis of its salt solutions and found to melt at 155° ± 1. Renz[5] states that indium oxide (In_2O_3) sublimes without melting when heated in an iridium dish, and distinguishes two varieties of this compound, one an amorphous modification soluble in acids and a second crystalline and insoluble form.

In the department concerned with the revision of the atomic weights of the elements, many observations of importance are to be recorded.

Guye and Mallet[6] discuss the experimental results obtained by Morley, and, after applying corrections to these average values, suggest the following: O = 15·8787, H = 1, or H = 1·00764, O = 16. The densities of sulphur dioxide and of oxygen have been determined by the application of the method used by Morley for hydrogen, giving the

[1] *J. Amer. Chem. Soc.*, 1904, **26**, 922.
[2] *Zeit. Elektrochem.*, 1904, **10**, 331.
[3] *Ber.*, 1904, **37**, 1135.
[4] *Ibid.*, 175; *Zeit. anorg. Chem.*, 1904, **39**, 119; *ibid.*, **40**, 280.
[5] *Ber.*, 1904, **37**, 2110.
[6] *Compt. rend.*, 1904, **138**, 1034.

weight of 1 litre of oxygen as 1·4292 grams, error $\frac{1}{3000}$, and of sulphur dioxide as 2·92664 grams with maximum error of $\frac{1}{10000}$ (Jacquerod and Pintza).[1]

The density of nitrous oxide and the determination of its volumetric and gravimetric composition have been utilised for the purpose of fixing the atomic weight of nitrogen, giving the value 14·011 (Rayleigh,[2] Guye and Pintza,[3] Jacquerod and Bogdan,[4] Guye and Bogdan [5]).

The revision of the atomic weight of rubidium made by Archibald,[6] who experimented with specially prepared chloride and bromide, gives 85·487 from the chloride, 85·483 from the bromide, and the means of both sets of determinations give 85·485.

The question of the atomic weight of beryllium is again revived. By the conversion of beryllium acetylacetonate into the oxide, Parsons [7] finds the value $9{\cdot}113 \pm 0{\cdot}0059$ (O = 16), whilst the same author obtains $9{\cdot}113 \pm 0{\cdot}0043$ from the amount of oxide yielded by the basic acetate, $Be_4O(C_2H_3O_2)_6$. Haber and Van Oordt [8] have investigated the influence of different salt solutions on the physical properties of beryllium hydroxide, and find [9] that the basic acetate formed by treatment of the hydroxide with glacial acetic acid is soluble in chloroform, a property which affords a means of separating it from the insoluble basic acetates of iron and aluminium. Tanatar [10] has suggested that beryllium is a quadrivalent element and that the basic acetate should be represented by the formula

$$Be(O{\cdot}C_2H_3O)_3O,Be(O{\cdot}C_2H_3O)_3\,;$$

further, that the atomic weight is 18·2, which, when multiplied into the specific heat at low temperatures, gives an atomic heat of 6·8—7·4. Attempts to produce beryllium alums containing rubidium and cerium sulphates have been unsuccessful. Possibly the grounds for this suggestion of Tanatar may find an explanation in the facts recorded by Pollok [11] in his paper entitled "The Composition of Beryl." Employing beryl obtained from Limoges, pure beryllia was prepared; this was mixed with sugar charcoal heated in a stream of chlorine and the operation conducted in such a way as to allow of the separation of the more volatile chlorides from the less volatile. The proportion of chlorine in these separate portions gave equivalents differing from one another to such an extent as to justify the conclusion that the beryl contains, associated with the beryllium, an element of high atomic

[1] *Compt. rend.*, 1904, **139**, 129.
[2] *Proc. Roy. Soc.*, 1904, **74**, 181.
[3] *Compt. rend.*, 1904, **139**, 677.
[4] *Ibid.*, 49.
[5] *Ibid.*, **138**, 1494.
[6] *Trans.*, 1904, **85**, 776.
[7] *J. Amer. Chem. Soc.*, 1904, **26**, 721.
[8] *Zeit. anorg. Chem.*, 1904, **40**, 465.
[9] *Ibid.*, **38**, 377.
[10] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 82.
[11] *Trans.*, 1904, **85**, 1630.

weight; from the quoted results, the atomic weight must be much higher than that of beryllium. The author considers that his experiments explain the anomalous specific heat observed for beryllium, as the metal used would be likely to contain both elements. In fact, whilst determining the heat of formation of beryllium chloride by dissolution of the metal in hydrochloric acid,[1] the author obtained "varying numbers for different samples of metals prepared from distinct portions of glucina," all of which appeared to be perfectly pure. The results of these observations led him to undertake this examination into the nature of glucina.

Moissan[2] has re-determined the relative density of fluorine, using Regnault's method, to test the validity of Brauner's suggestion that the activity of fluorine might be due to the presence in it of atomic particles, which the value 1·26, as opposed to the theoretical 1·316, appeared to justify. The mean of four determinations gives 1·31 (air = 1); which is sufficiently near to make Brauner's assumption inadmissible.

The value to be assigned to the atomic weight of iodine forms the subject of two publications, one, by G. P. Baxter,[3] in which results are given of the determination of the ratios: (1) silver to silver iodide, (2) silver to iodine, (3) silver chloride to silver iodide. The means of all these experiments gives the value 126·975 (O = 16), and incidentally the value 35·467 for chlorine is confirmed. The second publication is that of Köthner and Aeuer,[4] who purified the iodine employed by first converting it into ethyl iodide, from which, after purification, hydriodic acid was prepared and converted into silver iodide, thus giving the value 126·026 (H = 1).

By weighing the water produced from the hydrogen evolved in the dissolution of aluminium in hydrogen chloride, the value 27·05 has been found by Kohn-Abrest[5] for the atomic weight of aluminium; whilst from the weight of oxide formed from the metal 27·09 is obtained as the atomic weight (H = 1).

From the analysis of ferrous bromide made by the action of a current of nitrogen and hydrogen bromide on heated metallic iron, Baxter[6] finds the atomic weight of iron to be 55·85 (O = 16), whilst by the reduction of ferric oxide in hydrogen the value 55·883 is obtained.

In this connection, that is, the determination of the stoichiometric values of elements and compounds, may be mentioned the examination of the question of the vapour density of hydrazine hydrate by Scott,[7]

[1] Pollok, *Trans.*, 1904, **85**, 603.
[2] *Compt. rend.*, 1904, **138**, 728.
[3] *J. Amer. Chem. Soc.*, 1904, **26**, 1577.
[4] *Ber.*, 1904, **37**, 2536.
[5] *Compt. rend.*, 1904, **139**, 669.
[6] *Zeit. anorg. Chem.*, 1904, **38**, 232.
[7] *Trans.*, 1904, **85**, 913.

the results of which afford a complete refutation of the statements of Curtius and Schultz (1890). The hydrate (N_2H_4,H_2O) is shown to dissociate in a vacuum at 100°, the dissociation being complete at 143°; under atmospheric pressure at 183°, decomposition into ammonia and nitrogen sets in, and at still higher temperatures further resolution takes place. The nature of the surfaces with which the vapour is in contact exerts an influence on the initial temperature of decomposition and also on the rate of the change.

In reference to atomic weight determinations, the warning of the International Commission against the use of glass vessels in investigations of this kind finds a justification in the demonstration by Moissan and Siemens [1] that water heated with silicon in glass vessels is attacked with the liberation of hydrogen, whereas in platinum or quartz no such action is observed. This action arises from the alkali dissolved from the glass, which in turn interacts with the silicon, forming a silicate which decomposes into the dioxide and regenerates the alkali for further action.

An indication of the advance made during the past year in our knowledge of compounds of the elements may most conveniently be arrived at by discussing some of these under the headings of the groups in the periodic system.

I*A*.—A series of double compounds of rubidium and bivalent mercury, HgI_2,RbI, HgI_2,2RbI, has been described by Grossmann,[2] also the double thiocyanates, $Hg(SCN)_2$,RbSCN and

$$Hg(SCN)_2 2Rb(SCN)_2, \tfrac{1}{2}H_2O,$$

together with the cyanothiocyanate, $Hg(CN)_2Rb(SCN)$, which resembles very nearly the analogous pyridine compound,

$$Hg(CN)_2,C_5H_6N(SCN).$$

The specific gravities of the halides of lithium have been exactly determined by Baxter.[3] The production of sodium oxide by the interaction of the peroxide and the metal has been patented.[4]

From the standpoint of the phase rule, Fedotéeff [5] has examined the ammonia-soda process, concluding that it is better for solid or dissolved salt to be brought into contact with solid ammonium hydrogen carbonate than to operate as in the Solvay process.

I*B*.—The action of sulphuretted hydrogen on the double cyanides of copper and potassium shows that whilst the salts $[Cu_2(CN)_2H_2O]K$ and $Cu_2(CN)_4K_2$ are attacked, those having the formula $Cu_2(CN)_8K_6$ are not acted upon, and Treadwell and Von Griswald [6] conclude that this

[1] *Compt. rend.*, 1904, **138**, 939. [2] *Ber.*, 1904, **37**, 1258.

[3] *Amer. Chem. J.*, 1904, **31**, 558.

[4] Badische Anilin- & Soda-Fabrik, D.R.-P. 147933; Basler Chem. Fabrik, D.R.-P. 148784.

[5] *Zeit. physikal. Chem.*, 1904, **49**, 162. [6] *Zeit. anorg. Chem.*, 1904, **39**, 92.

is due to the formation of ions containing more than $Cu_2(CN)_4$, possibly $Cu_2(CN)_8$ or $Cu(CN)_6$. Solutions of copper in potassium cyanide, examined by the electrical method used in the investigation of solutions of complex silver salts by Bodländer and Eberlein,[1] are shown to contain chiefly the ions $Cu(CN)_4^{III}$, and to a less extent $Cu(CN)_3^{II}$[2]. A series of well-defined complex copper salts has been prepared by treating ammoniacal solutions of cupric salts with solutions of potassium or ammonium salts; for example, $[Cu(NH_3)_4](SCN)_2$ is formed when potassium thiocyanate is employed.[3] From experiments on the electrolytic transport in aqueous solutions of copper chloride, it is concluded that such solutions contain cathions of complexes containing water molecules, such as $[CuCl(H_2O)_3]$, which, with water at low temperature, act so as to form $[Cu(H_2O)_4]'' + Cl'$, a reaction reversed at higher temperatures.

The action of chloric acid on copper and the production of the basic chlorate of this metal are discussed by Brochet,[4] and the properties of crystallised copper iodates by Grainger and de Schulten.[5]

Normal silver chromate (Ag_2CrO_4) is formed from a soluble silver salt and a normal chromate, also by the action of water on silver dichromate.[6] Silver dihydrogen pyrophosphate, $Ag_2H_2P_2O_7$, is produced by the solution of silver pyrophosphate in pyrophosphoric acid and precipitation by alcohol or ether (Cavalier).[7]

II*A*.—The extension of the research on the action at high temperatures of manganese fluoride on calcium chloride, by which crystalline calcium fluoride and calcium fluorochloride are formed, has yielded under similar conditions the fluorides of barium and of strontium, also fluorochlorides, fluorobromides, and fluoroiodides of the metals of the alkaline earths.[8] Examples of the composition of these substances are afforded by the following formulæ: $BaCl_2,BaF_2$; $BaBr_2,BaF_2$; BaI_2,BaF_2. The study of the decomposition of mixtures of calcium carbonate and the carbonates of the alkali metals by heat at 1000° *in vacuo* shows that the mixed carbonates dissociate less readily than calcium carbonate, that the dissociation pressure is lower than that of calcium carbonate and higher than that of the alkali carbonate at the same temperature Lebeau has also obtained lime in the crystalline form, and proved that lithia and lime form isomorphous mixtures of regular octahedral crystals.[9] The production of calcium carbide when a mixture of fused calcium fluoride and calcium chloride is electrolysed, using a carbon

[1] *Zeit. anorg. Chem.*,1904, **39**, 197. [2] *Ibid.*, **41**, 359.
[3] *Ber.*, 1904, **37**, 1153.
[4] *Bull. Soc. chim.*, 1904, [iii], **31**, 287, **290**, 293.
[5] *Compt. rend.*, 1904, **139**, 201. [6] *Zeit. anorg. Chem.*, 1904, **41**, 68.
[7] *Compt. rend.*, 1904, **139**, 284.
[8] *Ibid.*, **138**, 197; *Ann. Chim. Phys.*, 1904, [viii], **1**, 337.
[9] *Compt. rend.*, 1904, **138**, 1496; *ibid.*, 1602.

cathode, has been observed by Moissan,[1] who has established the fact that lime is not attacked by carbon at the temperature of the oxy-hydrogen flame, but as crystals of calcium silicate are formed on the lime, Moissan[2] concludes that silica has a distinct vapour pressure at this temperature. The insolubility in water of barium sulphate prevents the hydration or hardening of this compound, but the solubility can be increased by the addition of solutions of aluminium chloride, ferric chloride, or ammonium nitrate, and Rohland[3] has used these to effect the hardening of barium sulphate.

II*B*.—Magnesium hydroxide suspended in water is dissolved by carbon dioxide, and from the solution alcohol precipitates the compound $MgCO_3,3H_2O$, the solid in suspension gradually acquiring the same composition.[4] The dissolution of this compound in solutions of potassium bicarbonate results in the formation of the compound

$$MgCO_3,KHCO_3,4H_2O.$$[5]

When the chromates of potassium or ammonium are added to solutions of zinc chloride, double chromates are produced, whereas with sodium chromate the basic compound $ZnCrO_4,3Zn(OH)_2$ is formed.[6] Briggs[7] has described the double chromates of nickel and magnesium with potassium, rubidium, and cerium of the type $M_2'M''(CrO_4)_2,6H_2O$, analogous to the magnesium double sulphates.

By methods similar to those employed in the study of solutions of copper salts, Kunschert[8] proves that the solutions of zinc salts in potassium or ammonium oxalates contain in concentrated solutions ions, $Zn(C_2O_4)_3$, and in dilute, $Zn(C_2O_4)_2$. The solutions in caustic soda contain the ions ZnO_2, which on hydrolysis form $HZnO_2'$ and OH^1, whereas the solutions in potassium cyanide contain $Zn(CN)_4$ and $Zn(CN)_3$.

Rây[9] has obtained mercuric nitrite by the interaction of mercuric chloride and silver nitrite; when heated at 100° *in vacuo*, this compound breaks up thus:

$$Hg(NO_2)_2 = HgO + N_2O_3\,;\quad Hg(NO_2)_2 = HgNO_3 + NO.$$

The hydrolysis of series of normal mercuric salts is proved by Cox[10] to yield basic salts intermediate between the normal salts and the oxide. The decomposition of mercurous nitrate is more complex than that of the mercuric salt; mercuric fluoride forms the oxide and hydrofluoric acid.

[1] *Compt. rend.*, 1904, **138**, 661; Bullier, *ibid.*, **138**, 904.
[2] *Ibid.*, **138**, 243.
[3] *Zeit. anorg. Chem.*, 1904, **38**, 311.
[4] *Chem. Zeit.*, 1904, **28**, 868.
[5] *Zeit. Elektrochem.*, 1904, **10**, 161.
[6] *Monatsh.*, 1904, **25**, 520.
[7] *Trans.*, 1904, **85**, 672.
[8] *Zeit. anorg. Chem.*, 1904, **41**, 337.
[9] *Trans.*, 1904, **85**, 523.
[10] *Zeit. anorg. Chem.*, 1904, **40**, 146.

III*A*.—For the production of crystallised boron, Kühne[1] recommends mixing boron trioxide with aluminium turnings and sulphur, the action to be started by applying a red-hot iron rod to a mixture of aluminium and sulphur; from the resultant mass, the aluminium sulphide is removed by dissolving in hydrochloric acid. Silicon can be obtained by substituting silica for the boron trioxide.

The study of the melting-point curves of mixtures of boron trioxide and the oxides of the alkaline earths indicates the existence of ortho-, meta-, pyro-, and di-borates of these elements.[2] From the investigation of the electrical conductivity of solutions of borax, Grünhut[3] concludes that borax is resolved on dissolution in water into boric acid and the metaborate; when carbon dioxide is passed into the cold solution, the metaborate decomposes and sodium hydrogen carbonate is formed; if boric acid is added to the solution saturated with carbon dioxide, some metaborate is reproduced in virtue of mass action.

III*B*.—When aluminium fluoride is fused with sodium sulphide, a mixture of sodium aluminofluoride and sodium thioaluminate is produced:

$$2Al_2F_6 + 6Na_2S = Al_2F_6,6NaF + Al_2S_3,3Na_2S.$$

This mixture, when electrolysed in the fused state, yields aluminium, sulphur, and sodium fluoride; the reactions are expressed as follows:

$$Al_2S_3,3Na_2S = 2Al + 3S + 3Na_2S.$$
$$Al_2F_6,6NaF + 3Na_2S = 2Al_2 + 3S + 12NaF.$$

On these reactions is based the following patented process: first, aluminium fluoride is formed from bauxite by the action of hydrofluoric acid, the fluoride being freed from iron and titanium by digestion with alumina. The sulphur produced in the above reactions can be used for the manufacture of the sulphuric acid required to prepare hydrofluoric acid from the sodium fluoride formed, the sodium sulphate resulting from this reaction being converted into sodium sulphide by heating with coal.[4]

By the action of barium chlorate on aluminium sulphate, the two hydrated aluminium chlorates $Al(ClO_3)_3,9H_2O$ and $Al(ClO_3)_3,6H_2O$ have been prepared and their behaviour when heated studied, from which it would appear that when slowly heated at 100° they decompose with explosive violence, yielding chlorine peroxide; when heated rapidly, chlorine is formed, and a residue of a basic perchlorate, $Al_2(ClO_4)_6,Al_2O_3$, left.[5]

[1] D.R.-P. 147871.
[2] Guertler, *Zeit. anorg. Chem.*, 1904, **40**, 337.
[3] *Zeit. physikal. Chem.*, 1904, **48**, 569.
[4] Gin, D.R.-P. 148627.
[5] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 468.

Mention should be made of Verneuil's[1] successful production of artificial rubies by heating alumina with a blowpipe flame, into which is blown a mixture of chromium sesquioxide and alumina.

A number of compounds of aluminium chloride and organic substances containing oxygen have been prepared by Walker and Spencer[2] by the addition of aluminium chloride to the organic substances in presence of carbon disulphide. These compounds consist of equimolecular proportions of the chloride and organic compound, for example, $AlCl_3,(C_2H_5)_2O$, save in the instance of methyl mandelate and acetic acid, which form compounds containing four molecules of the chloride.

IV*B*.—Silicon hydride is formed by the direct union of the elements at the temperature of the electric arc. Further, Dufour[3] has demonstrated the reduction of silica by hydrogen. Moissan and Siemens[4] have investigated the solubility of silicon in molten metals, for example, zinc, lead, silver, tin, and aluminium; from the solution in silver, part of the silicon separates out in crystalline form, which is soluble in hydrofluoric acid.

Lead metasilicate[5] heated in a current of hydrogen yields a "silicite,' which is also formed together with metallic lead from the orthosilicate, from which it is concluded that two classes of lead silicates exist: (1) those containing the acid radicle in excess and yielding a "silicite"; (2) those containing the basic radicle in excess, which yield a "silicite" and metallic lead; these views being explained by the following formulæ:

$$\left(\begin{array}{l}|\\ Si<\begin{array}{l}O\cdot Pb\\ O\cdot O\end{array}\\ |\end{array}\right)_n = \left(Si<\begin{array}{l}O\\ O\end{array}>Pb\right)_n + O_n.$$

$$\left(\begin{array}{l}|\\ Si<\begin{array}{l}O\cdot Pb\cdot O\\ O\cdot O-Pb\end{array}\\ |\end{array}\right)_n = \left(Si<\begin{array}{l}O\\ O\end{array}>Pb\right)_n + {}_nO_2 + {}_nPb.$$

Chlorostannic acid (H_2SnCl_6), bromostannic acid (H_2SnBr_6), and iodostannic acid (H_2SnI_6) undergo hydrolysis, which is most complete in the case of the last-named acid; pyridine and quinoline compounds of the iodostannic acid are described by Rosenheim and Arons.[6]

Of the stannichlorides, the following are described by von Biron:[7] Rb_2SnCl_6, $ZnSnCl_6,6H_2O$, $FeSnCl_6,6H_2O$, $SrSnCl_6,4H_2O$, and $Li_2SnCl_6,6H_2O$.

Attempts to prepare corresponding cadmium, copper, silver, lead,

[1] *Ann. Chim. Phys.*, 1904, [viii], **3**, 20.
[2] *Trans.*, 1904, **85**, 1106.
[3] *Compt. rend.*, 1904, **138**, 1040.
[4] *Ibid.*, 657.
[5] Simmonds, *Trans.*, 1904, **85**, 681.
[6] *Zeit. anorg. Chem.*, 1904, **39**, 170.
[7] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 489.

and thallium compounds were unsuccessful. The author regards the stannichlorides as analogous to the platinichlorides, and Bellucci and Parravano,[1] discussing the constitution of the stannates, express the view that they may be regarded as derivatives of the acid $H_2Sn(OH)_6$, analogous to $H_2Pt(OH)_6$.

The solutions of lead halides and sodium thiosulphate are sensitive to light, and on exposure to bright light deposit red precipitates, such as $Pb_4S_5Cl_2$ from the chloride, and $Pb_3S_4I_2$ from the solution of the iodide, whereas in diffused light or in the dark the sulphide is deposited.[2] Strömholm[3] describes a series of basic lead salts produced by the action of alkali salts on lead hydroxide suspended in water. Lead carbonate is formed by the action of ammonium carbonate in the cold on a solution of lead chloride, and on boiling is converted into the basic salt, $2PbCO_3,Pb(OH)_2$, which is also formed when lead carbonate is boiled with sodium sulphate or chloride.[4]

V*A*.—Ruff and Geisel[5] have studied the properties of nitrogen sulphide, N_4S_4, which is produced from sulphur tetrachloride and ammonia in accordance with the equation:

$$12SCl_4 + 16NH_3 = 3N_4S_4 + 48HCl + N_2.$$

It is attacked by dry hydrogen chloride, yielding ammonia, but no nitrogen; liquid ammonia dissolves it, giving solutions which with lead iodide form PbN_2S_2,NH_3, and with mercuric iodide HgN_2S,NH_3. The authors conclude that the following is the most satisfactory representation of its constitution:

$$S{:}S\ll\begin{matrix}N\cdot S{:}N\\ N\cdot S{:}N\cdot\end{matrix}$$

This substance, when treated with ammonia, forms $N{:}SNH_2$ and $S{:}S(NH_2)_2$, the first yielding mercuric thiodi-imide, $N{:}S\cdot NHg$, and the latter lead thiodi-imide, $S{:}S\ll\begin{matrix}N\\ N\end{matrix}>Pb$.

Herrenschmidt[6] describes the industrial production of vanadium and some of its alloys, which is of interest in association with the use of this metal in the manufacture of special steels. The vanadium is obtained in the slag formed by fusion of lead vanadate from the Santa Marta mines in Spain with sodium carbonate and charcoal. The slag contains sodium vanadate, aluminate, and silicate together with iron oxide. It is obtained as vanadic acid by oxidation in the fused state with atmospheric oxygen, then extracting with water and precipitating by sulphuric acid. Ferrovanadium containing 33 per cent. of vanadium

[1] *Atti R. Accad. Lincei*, 1904, [v], **13**, 11, 307; *ibid.*, [v], **13**, 11, 324.
[2] Hofmann and Wölff, *Ber.*, 1904, **37**, 249.
[3] *Zeit. anorg. Chem.*, 1904, **38**, 429.
[4] Salvadori, *Gazzetta*, 1904, **34**, [i], 87.
[5] *Ber.*, 1904, **37**, 1573.
[6] *Compt. rend.*, 1904, **139**, 635.

is formed by the ignition in the electric furnace of the precipitate formed by treating sodium vanadate with ferrous sulphate and sodium carbonate. Nickel vanadium containing 50 per cent. of vanadium is formed by reduction of a mixture of vanadium pentoxide and nickel oxide.

Hall,[1] in describing the production of oxides of columbium and of tantalum from columbite (Haddam, Conn.), also discusses the use of sulphur chloride in the formation of chlorides of the metals from their oxides, showing that both columbium and tantalum pentoxides yield the pentachlorides; further, titanic oxide, aluminia, and ferric oxide yield volatile chlorides when heated with sulphur chloride, whilst tungstic, vanadic, and molybdic oxides yield the oxychlorides; zirconium and tin dioxides give the chlorides only after prolonged heating, whereas silica and boron trioxide do not react with sulphur chloride.

VB.—Arsenamide, $As(NH_2)_3$,[2] is formed by the action of gaseous ammonia on the trichloride, tribromide, and tri-iodide of arsenic at $-30°$ to $-40°$; it is resolved by water into arsenic trioxide and ammonia. At temperatures above 0°, it decomposes, and at 60° is completely resolved into the imide, $2As(NH_2)_3 = As_2(NH)_3 + 3NH_3$.

The imide at 250° forms the nitride, AsN, and this at higher temperatures yields nitrogen and arsenic.

When phosphorus trichloride[3] is led by means of hydrogen into liquid ammonia at $-78°$, the following reaction takes place:

$$PCl_3 + 14NH_3 = 3(NH_4Cl,3NH_3) + NH{:}PNH_2.$$

At 0° the ammoniacal ammonium chloride decomposes, and between 0° and 100° a further decomposition results in the production of the imide $P_2(NH)_3$. Boron bromide and ammonia react in a somewhat similar manner, giving, however, the imide $B_2(NH)_3$ in the first reaction.

As a reagent for phosphine, arsine, and stibine, Lemoult[4] suggests the use of a solution of mercuric iodide in potassium iodide, with which each of the gases forms a characteristic precipitate.

Some salts of trithio-oxyarsenic acid are described by McCay and Foster[5] in the production of which the sodium salt, $Na_3AsOS_3,11H_2O$, is used. This salt is produced by treating freshly precipitated arsenic pentasulphide with magnesia, removing the magnesia with caustic soda, and precipitating the salt with alcohol.

Bismuth tetroxide is formed when the trioxide is oxidised with alkaline potassium ferricyanide, whereas when oxidised with chlorine

[1] *J. Amer. Chem. Soc.*, 1904, **26**, 1235. [2] Hugot, *Compt. rend.*, 1904, **139**, 54.
[3] Joannis, *ibid.*, 364. [4] *Ibid.*, 478.
[5] *Ber.*, 1904, **37**, 573; *Zeit. anorg. Chem.*, 1904, **41**, 452.

in presence of an alkali both the tetroxide and the pentoxide are formed.[1]

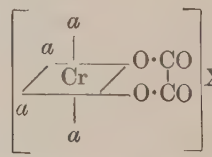
VI*A*.—Since the stability of endothermic compounds is greater the higher the temperature, the conversion of oxygen into ozone at high temperature should be possible. Clement [2] has, however, demonstrated this not to be the case, and attributes the reported formation of ozone at high temperatures to the formation of nitric oxide produced from the nitrogen present as impurity in the oxygen.

Pfeiffer,[3] by the investigation of the compounds of chromium and ethylenediamine, has brought to light a series of complex substances having the general formula $[En_2\overset{+}{C}rX_2]\overset{-}{X}$, in which formula "En" is used to represent the ethylenediamine residues; in these compounds, only one X is in the ionic state. The compound $[EnCr(SCN)_2]SCN$ is formed by the action of $K_3[Cr(SCN)_6]$ on ethylenediamine. It exists in two isomeric forms, namely, the α- and β-modifications; corresponding chlorine compounds, $[En_2CrCl_2]Cl$, have been prepared, one of which is green and the other violet. The author explains the isomerism as arising from different stereometric arrangements, for which the following formulæ are proposed, representing a *cis*- and *trans*-modification:

cis. *trans.*

In these formulæ, the chromium occupies the centre of a regular octahedron, and is attached to ethylenediamine residues represented by *a*, X representing an electro-negative acid group, for example, SCN.

The *cis*-form can be distinguished from the *trans*-form by it alone producing a closed ring with dibasic acid radicles. Experimentally it has been found that the α-modifications which are green do not form oxalates, such as the following:



whereas the β-modifications do, hence the *cis*-type is associated with the violet-coloured compounds.

[1] Hauser and Vanino, *Zeit. anorg. Chem.*, 1904, **39**, 381.
[2] *Ann. Physik*, 1904, [iv], **14**, 334. [3] *Ber.*, 1904, **37**, 4255.

Hofmann and Hiendlmaier[1] prepare the ammonium salt of chromatodiper acid by the action of ammonia and hydrogen peroxide on chromic hydroxide; it has the yellow colour of the sexavalent chromium compounds, and when treated with acids decomposes, giving only transiently the blue of perchromic acid. The authors regard the perchromates as containing heptadic chromium, thus: $CrO_3{\cdot}O{\cdot}O{\cdot}NH_4$, whereas the salts of chromatodiper acid contain sexavalent chromium, for example, $CrO_2\begin{matrix}<O{\cdot}O{\cdot}NH_4\\ O{\cdot}O{\cdot}NH_4\end{matrix}$ and the conversion of the reddish-yellow chromates to blue perchromates is considered as analogous to the change from manganates to permanganates.

A new molybdenum carbide, MoC, has been obtained by Moissan by heating in the electric furnace a mixture of molybdenum, carbon, and aluminium.[2]

Briggs[3] has obtained a series of ammoniacal double chromates and molybdates of the general formula $M_2'M''(RO_4),2NH_3$, in which M′ is either potassium or ammonium, M″ may be copper, zinc, or cadmium, and R is either chromium or molybdenum. They are compounds of considerable stability, parting with ammonia at temperatures about 200°. Tungsten does not form compounds of this type, but ammonio-copper and ammonio-zinc tungstates have been prepared. The solution of molybdic acid in hydrochloric acid appears to contain chloromolybdic acid, of which Weinland and Knoll have prepared the cerium, rubidium, pyridine, and quinoline salts.[4]

Schaeffer[5] has added much to our knowledge of the compounds of tungsten, demonstrating the existence of only one potassium tungsten bronze, which has the formula $K_2W_4O_{12}$. Several paratungstates are described, and it is also shown that in the electrolysis of a solution of the normal sodium or potassium tungstate at the anode there is first formed the paratungstate, $5Na_2O,12WO_3$, and subsequently the meta-tungstate, $Na_2O,4WO_3$.

VI*B*.—Harpf[6] finds that sulphur is oxidised at the ordinary temperature, especially in sunlight. The production of sulphur dioxide sufficiently explains the antiseptic properties of the element, without the suggestion that it is due to hydrogen peroxide produced by plants.

Sulphur tetrachloride and the compounds it forms with other chlorides have already been referred to. The production of alkali hyposulphites by the action in presence of ether of sulphur dioxide on sodium or potassium alloyed with lead or mercury is the subject of a patent. The compounds so obtained are very stable in contact with

[1] *Ber.*, 1904, **37**, 1663; *ibid.*, 3405.
[2] *Compt. rend.*, 1904, **138**, 1556.
[3] *Trans.*, 1904, **85**, 677.
[4] *Ber.*, 1904, **37**, 569.
[5] *Zeit. anorg. Chem.*, 1904, **38**, 142.
[6] *Ibid.*, **39**, 387.

air.[1] Bucherer and Schwalbe [2] attribute the following constitution to sodium hyposulphite, $O<\begin{matrix}S(HO)\cdot ONa\\ |\\ S(HO)\cdot ONa'\end{matrix}$, which includes the one molecule of water of constitution this compound contains when salted out from its solutions. The electrolytic production of hyposulphites has been the subject of several papers.[3] Experimenting with aqueous solutions of sodium thiosulphate, Thatcher [4] shows the compound to be oxidised forming tetrathionate when the solution is neutral or faintly alkaline, but when the solution is acid or strongly alkaline, sulphur, sulphite, and sulphate are formed.

A number of well-defined crystalline polysulphides of the heavy metals have been obtained by Hofmann and Höchtlen [5] with an ammoniacal solution of a copper salt. Ammonium persulphide gives a crystalline precipitate, CuS_4NH_4, which is regarded as the cuproso-ammonium salt of $H\cdot S_4H$. From platinic chloride, the compound $PtS_{15}(NH_4)_2,2H_2O$ is obtained; this is a derivative of H_2S_5, having the constitution $S_5{:}Pt{:}[S_5(NH_4)]_2$. Thallous chloride yields black crystals of Tl_2S_5. Auric chloride and ammonium persulphide give yellow crystals, AuS_3NH_4, whilst the chloride in ethereal solution with sulphuretted hydrogen gives Au_2S_3. Iridium chloride ($IrCl_3$) yields $IrS_{15}(NH_4)_3$. Whilst with bismuth chloride in aqueous solutions the sulphide is formed, in alcoholic solutions a compound crystallising in black prisms of the composition $Bi_2S_{14}O_6N_4H_{16}$ is produced, which appears to contain thiosulphate groups; for it the formula $\begin{matrix}NH_4S_4\\ NH_4S_2O_3\end{matrix}>Bi\cdot S\cdot S\cdot Bi<\begin{matrix}NH_4S_4\\ NH_4S_2O_3\end{matrix}$ is suggested.

With regard to tellurium, it is stated that potassium tellurate is produced by the oxidation of tellurium dioxide in presence of caustic potash with hydrogen peroxide.[6] The electrolysis of telluric acid solution in presence of potassium cyanide yields a brownish-violet solution of colloidal tellurium; the replacement of the cyanide by ammonium oxalate yields a blue hydrosol.[7]

The production of the hydrides of sulphur, selenium, and tellurium by the direct union of the elements has been established by F. Jones.[8]

VII*A*.—It would appear that the manganates of the alkaline earths hitherto described are mixtures, and that pure compounds of

[1] Badische Anilin- & Soda-Fabrik (D.R.-P. 148125).

[2] *Zeit. angew. Chem.*, 1904, **17**, 1447.

[3] Elbs and Becker, *Zeit. Elektrochem.*, 1904, **10**, 361; Friesner, *ibid.*, 265; Frank, *ibid.*, 450.

[4] *Zeit. physikal. Chem.*, 1904, **47**, 641.

[5] *Ber.*, 1904, **37**, 245, and *ibid.*, 1903, **36**, 3540.

[6] Gutbier and Wagenknecht, *Zeit. anorg. Chem.*, 1904, **40**, 260.

[7] Gutbier and Resenscheck, *ibid.*, 264.

[8] *Mem. Manchester Phil. Soc.*, 1904, **48**, xvi, 1.

the type $M_3Mn_2O_8,H_2O$ are formed by fusing at 180° to 280° mixtures of the hydroxides of the alkaline earths with nitre and potassium permanganate; these substances are mangani-manganates.[1]

VII*B*.—Moissan[2] has redetermined the physical constants of phosphorus trifluoride, pentafluoride, and oxyfluoride. Titanium fluoride, TiF_4, is formed, according to Emrich,[3] by the decomposition by heat of barium titanofluoride, $BaTiF_6$. Ruff and Plato[4] have extended their investigations of fluorides prepared by the action of dry hydrogen fluoride on the corresponding chlorides: TiF_4, a liquid boiling at 284°; SnF_4, a hygroscopic, crystalline solid boiling at 705°; SbF_5 is a viscid liquid (b. p. 155°); with the trifluoride, it forms Sb_3F_{11} or $SbF_5 2SbF_3$, boiling at 390°, also Sb_6F_{20}, which boils at 384°. The molecular volumes of the fluorides are considerably less than those of the corresponding chlorides.

The action of a mixture of chlorine and sulphur chloride on the heated oxides is proposed by Matignon and Bourion[5] as a general method for the production of anhydrous chlorides; by this means they have prepared chlorides of silicon, aluminium, chromium, iron, zinc, manganese, nickel, and cobalt, also vanadium tetrachloride and vanadium trichloride. Vanadic acid is converted by this mixture in the cold into the oxychloride, $VOCl_3$. Tungsten oxide yields both WO_2Cl_2 and $WOCl_4$. Barium sulphate, calcium sulphate, and calcium carbonate are converted quantitatively into the chlorides. Boron chloride cannot be obtained in this way.

By noting the action of the vapours on papers moistened with potassium iodide and starch, Fireman and Portner[6] find that phosphorus pentachloride commences to dissociate at 157—158°, ferric chloride at 122—123°, cupric chloride at 344°, and chromic chloride at 355°. When certain metallic chlorides are heated in sealed tubes with ammonium chloride at 380—410°, those which dissociate more or less readily are reduced to a lower stage of chlorination and nitrogen is produced, whereas others combine to form double compounds with ammonium chloride.[7] From the experiments of Gooch and McClenahan,[8] it appears that when $BaCl_2,2H_2O$, $MgCl_2,6H_2O$, and $AlCl_3,6H_2O$ are heated in dry hydrogen chloride, in some cases dehydration is favoured, in others this action is inhibited. E. Müller[9] shows that potassium periodate is

[1] Auger and Billy, *Compt. rend.*, 1904, **138**, 500.
[2] *Ibid.*, 789.
[3] *Monatsh.*, 1904, **25**, 907.
[4] Ruff, Plato and Graf, *Ber.*, 1904, **37**, 673.
[5] *Compt. rend.*, 1904, **138**, 631 and 760.
[6] *J. Physical Chem.*, 1904, **8**, 500.
[7] Fireman, *J. Amer. Chem. Soc.*, 1904, **26**, 741.
[8] *Amer. J. Sci.*, 1904, [iv], **17**, 365.
[9] *Zeit. Elektrochem.*, 1904, **10**, 753.

formed in the electrolysis of potassium iodate solutions made alkaline with caustic potash containing 0·1 per cent. of potassium chromate; further, that the yield is greatly increased by the presence of a fluoride. As to the patented application of hydrofluoric acid for the purpose of increasing the yield of chlorates in the electrolysis of alkali chlorides, it is shown by Foerster and Müller [1] that hydrofluoric acid has no special advantage, acidification by any acid being as efficient.

According to Tissandier, metallic iron heated at 900° in a stream of carbon dioxide is converted into ferrous oxide, whilst Donau [2] finds with the dry gas at 1200° that magnetite is formed, and when so produced is magnetic and crystalline.

Hydrated cobalt chloride, $CoCl_2,6H_2O$, dissolves in ethylene glycol, forming a violet-purple solution which becomes blue on heating; further, this solution is acted on by light, becoming bluish-violet after several weeks' exposure.[3] These observations are made by Oechsner de Coninck, who also states that nickel and cobalt oxides are converted into their sulphates by crushing in a mortar with sodium hydrogen sulphate.[4]

Nickel carbonyl is more efficiently prepared by working under a pressure of 2—100 atmospheres, the formation then taking place under conditions which allow of heat being applied to accelerate the reaction.[5] Dewar and Jones [6] have described the action of the halogens and several active inorganic substances on nickel carbonyl, showing that this compound usually breaks up so as to form carbon monoxide and nickel compounds with the reagents employed; the following may be taken as typical: $Ni(CO)_4 + Cl_2 = NiCl_2 + 4CO$. In no instance was the production of compounds of carbon monoxide observed.

Both gold and platinum are attacked under the influence of light by fuming hydrochloric acid in presence of air; the action is favoured by the presence of a trace of manganese chloride; in the absence of light there is no action.[7]

L. Wöhler [8] finds that whilst platinum forms only the two oxides PtO_2 and PtO, there are several hydroxides. Platinic oxide is both an acidic and basic oxide, whilst platinous oxide is essentially acidic. Platinic hydroxide is regarded as $H_2Pt(OH)_6$, and from it the following hydrates have been prepared: $PtO_2,3H_2O$, $PtO_2,2H_2O$, and PtO_2,H_2O, the last of which is insoluble in hydrochloric acid or *aqua regia*.

Potassium platinochloride, K_2PtCl_4, is technically prepared from the

[1] *Zeit. Elektrochem.*, 1904, **10**, 781.
[2] *Monatsh.*, 1904, **25**, 181.
[3] *Bull. Akad. Roy. Belg.*, 1904, **6**, 803; *ibid.*, 832.
[4] de Coninck, *ibid.*, 833.
[5] Dewar, D.R.-P. 149959.
[6] *Trans.*, 1904, **85**, 203.
[7] Berthelot, *Compt. rend.*, 1904, **138**, 1297.
[8] *Zeit. anorg. Chem.*, 1904, **40**, 423.

product of reduction of hydrogen platinichloride with sulphur dioxide; the reduction of potassium platinichloride by potassium oxalate takes effect only in presence of iridium, which acts as a catalytic agent.[1]

Howe,[2] in continuation of an investigation on the compounds of ruthenium, describes the preparation of chlororuthenates of the type $X_2Ru(OH_2)Cl_5$ and their isomerides, the chlororuthenites, X_2RuCl_5,OH_2; the former of these, when treated with chlorine, yield chlororuthenates such as K_2RuCl_6; corresponding bromide compounds are also described.

Iridium sesquisulphate, $Ir_2(SO_4)_3,xH_2O$, forms a series of well-defined alums with alkali sulphates, and also thallous sulphate.[3]

Many observations[4] have been made on the properties of colloidal metals, especially of gold and silver; for the production of colloidal salts of the latter, Paal and Voss[5] recommended the use of alkali protalbates, or lysalbates, the latter of which can be formed by the action of caustic alkali on egg-albumen and dialysing to remove excess of alkali. Castoro,[6] by the addition of acrolein to hot faintly alkaline solutions of gold chloride, has obtained gold hydrosols, varying in colour from sky-blue, amethyst, violet, pink, or purple, according to the state of dilution. With allyl alcohol, violet and ruby-red solutions are obtained. Hydrosols of the metals of the platinum group can be similarly produced.

A considerable number of interesting communications have been made on the subject of the formation and constitution of alloys and amalgams, both the study of the curves of melting points of mixed metals, as also the micrographical investigation, yielding valuable information. Moissan and O'Farrelley[7] show that binary alloys of metals which do not form carbides may be fractionally distilled in the electric furnace, and that copper, zinc, cadmium, lead, and tin may be completely or partially separated in this way. Zinc and cadmium may be separated from their alloys with copper, the alloys of copper and lead behaving like ether and water; tin and lead comport themselves like mixtures of alcohol and water, and leave a residue of pure tin, whilst copper and tin alloys behave like formic acid and water, yielding an alloy of constant boiling point containing 60 per cent. of tin.

Of special interest is the application of vanadium in the manufacture of steels, the constitution and properties of which have

[1] Klason, *Ber.*, 1904, **37**, 1360.

[2] *J. Amer. Chem. Soc.*, 1904, **26**, 543; *ibid.*, 942.

[3] Marino, *Zeit. anorg. Chem.*, 1904, **42**, 213.

[4] Hanriot, *Compt. rend.*, 1904, **138**, 1044; Gutbier and Resenscheck, *Zeit. anorg. Chem.*, 1904, **39**, 112; Paal and Amberger, *Ber.*, 1904, **37**, 124.

[5] *Ber.*, 1904, **37**, 3862.

[6] *Zeit. anorg. Chem.*, 1904, **41**, 126.

[7] *Compt. rend.*, 1904, **138**, 1659.

been studied by Guillet,[1] who, from their microstructure, forms three classes of such steels: (1) Those containing 0·2 per cent. of carbon and less than 0·7 per cent. of vanadium, the structure of which resembles that of ordinary steel; (2) those having from 0·2 to 0·8 per cent. of carbon and from 0·7 to 3 per cent. of vanadium, exhibit perlite structure; (3) those containing more than 3 per cent. of vanadium, in all the carbon exists as vanadium carbide or double carbide of vanadium and iron. The vanadium steels are all sensitive to thermal treatment, and their mechanical properties are greatly influenced by such treatment. Guillet's experiments on the cementation of carbon and special steels show that this process is influenced by the presence of other elements than carbon; the rate of cementation is increased by manganese, chromium, tungsten, and molybdenum, whilst nickel, titanium, silicon, aluminium, or tin retard the action. Experimenting with steels containing γ-iron, and also nickel and manganese, Guillet records interesting observations showing that carbon is dissolved by γ-iron at the ordinary temperature.

P. Phillips Bedson.

[1] *Compt. rend.*, 1904, **138**, 367, 1600; **139**, 426, 519, 540.

ORGANIC CHEMISTRY—ALIPHATIC DIVISION.

Speaking generally of the work done in the aliphatic series of carbon compounds during the year, it cannot be said that the period has been remarkable for any very striking discovery or for the initiation of any important new departure; the aim of the investigations has rather been directed towards the extension and amplification of the epoch-marking researches which have been accomplished within the last ten or fifteen years.

In view of the enormous amount of work which has been done, it would of course be altogether impossible to give anything like a comprehensive account; the mere titles of the papers and authors' names alone would fill a very considerable portion of the allotted space; even to make any appropriate selection from the papers which are likely to be of more general interest is no easy task since, notwithstanding this limitation, many highly interesting and important communications have to remain without notice.

In many of the references which are included it has only been found possible to give the merest indication as to the nature of the work; in others, such as the applications of Grignard's reaction, the chemistry of the carbohydrates and the polypeptides, it has been considered necessary, in view of the increasing importance of the subjects, to make the accounts more complete.

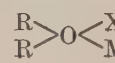
Grignard's Reaction.

Barbier, in 1899, appears to have been the first to suggest the substitution of metallic magnesium for zinc in certain synthetical operations, such as the formation of tertiary alcohols from ketones by the action of alkyl halides in presence of the metal. In 1900, Grignard published a general method for the synthesis of alcohols and hydrocarbons, which consisted in first preparing the "reagent" by the action of magnesium turnings on an alkyl halide in presence of perfectly dry ether, and using this to act on an aldehyde or ketone. Although the results are in many cases quite analogous to those obtained by the use of organo-zinc compounds, the preparation of the

reagent and simplicity of working details offer very great advantages over the older method, and the applications are much wider. Almost all classes of oxygen-containing organic compounds have been synthesised by this method; Grignard, for example, used it in the first instance for preparing primary, secondary, and tertiary alcohols, carboxy-acids, hydroxy-acids, and hydrocarbons; whilst others, such as Valeur, Blaise, Tissier, and Tschitschibabin, have by its means synthesised glycols, ketones, aldehydes, and ketonic acids. Thio-acids and substituted hydroxylamines have also been obtained by use of the reaction, and very many later examples of its application will be found in the accounts given below.

The formation of the "reagent" is generally expressed by the change $RX + Mg = R{\cdot}Mg{\cdot}X$, and its reactions can, as a rule, all be satisfactorily represented as being due to the latter compound. It seems probable, however, that the initial change is less simple and that the compound RMgX only represents the final stage, since the nature of the solvent evidently plays an important part.

From the earlier experiments, it appeared that ethyl ether was the only efficient solvent, and Grignard considered that the initial compound was of the type $RMgX,Et_2O$, in which the molecule of ether is "firmly attached" to the organo-magnesium halide. Baeyer and Villiger, on the other hand, regard this initial product as an oxonium compound, the four groups being linked to quadrivalent oxygen:

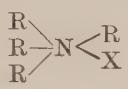


Later investigations have shown that certain other solvents may be substituted for ethyl ether; Hibbert and Sudborough [1] have successfully used amyl ether, and Tschelinzeff [2] has brought about the action with dimethylaniline as solvent. Bruhl, Oerdt, and Malmgren had also obtained certain organo-magnesium compounds using xylene as a solvent, but in this case a higher temperature seems to be necessary. Tschelinzeff has more recently [3] made a further study of this question as to the part played by the solvent; with regard to ether, he considers that its function is to dissociate or sever the linking between the halogen and alkyl groups, and that the latter then react with the elements of ether to give an oxonium compound, $R_2{:}O{:}RX$, which by the action of magnesium is converted to $R_2{:}O{:}MgR{\cdot}X$. In support of this view he draws attention to similar cases in which ether causes a disruption of the linking in simple halides, as a result of which more complex compounds may arise.[4]

[1] *Trans.*, 1904, **85**, 933. [2] *Ber.*, 1904, **37**, 2084. [3] *Loc. cit.*, p. 4534.

[4] Compare Klobukoff, *Zeit. physikal. Chem.*, 1889, **3**, 429 and 476; Friedel, *Bull. Soc. chim.*, 1900, [ii], **24**, 166; Archibald and McIntosh, *Trans.*, 1904, **85**, 919.

Still more interesting is his conclusion that, in the reactions which take place at a low temperature, the ether acts catalytically; using an otherwise inert solvent such as benzene, he finds that the formation of an organo-magnesium halide takes place if an ether is added even in mere traces, and that the quantity formed is disproportionately great in comparison with the amount of ether employed. Anisole, owing to its lesser volatility, is more suited for the observation of these effects than ethyl ether, although the influence of the latter was confirmed. The author further shows that tertiary amines also act catalytically, and that their influence is still more energetic than that of ether. The changes are explained in a similar way, the alkyl-halogen linking being severed and an intermediate product formed, which in this case is the quinquevalent nitrogen compound:



F. and L. Sachs have, in fact, shown [1] that tertiary amines combine with organo-magnesium halides to give additive compounds; although these on hydrolysis yield the original amine, they are themselves so "strongly bound" that they do not show the reactions of the amine. This catalytic influence of tertiary amines, such as dimethyl-aniline, can be made use of in the practical working of Grignard's reaction when benzene is employed as solvent.

Tschelinzeff in another communication [2] draws attention to a general similarity between the reactions of organo-magnesium halides on certain groups of oxygen and nitrogen compounds; the nature of such analogy may be gathered from the following few examples:

$$\begin{cases} H\cdot OH + RMgX = OH\cdot MgX + RH. \\ H\cdot NH_2 + RMgX = H\cdot NH\cdot MgX + RH. \end{cases}$$

$$\begin{cases} R\cdot C\lessdot{O \atop H} + 2R'MgX = R\cdot C(O\cdot MgX)(R')(O\cdot MgX) \longrightarrow R\cdot COR'. \\ R\cdot C\lessdot{O \atop NH_2} + 2R'MgX = R\cdot C(O\cdot MgX)(R')(NH\cdot MgX) \longrightarrow R\cdot COR'. \end{cases}$$

$$\begin{cases} OC{:}O + RMgX = O{:}CR\cdot O\cdot MgX \longrightarrow O{:}CR\cdot OH + OH\cdot MgX. \\ OC{:}NR + R'MgX = NR{:}CR'\cdot OMgX \longrightarrow O{:}CR'\cdot NHR + OH\cdot MgX. \end{cases}$$

Grignard's reaction has been employed also in the preparation of alkyl derivatives of elements other than carbon; it is shown, for example, by Pfeiffer and Schnurmann [3] that compounds such as stannic tetra-ethide or -phenide may be advantageously prepared by

[1] *Ber.*, 1904, **37**, 3089. [2] *Ibid.*, 2081. [3] *Ibid.*, 319.

the action of magnesium ethyl bromide on the halogen compounds of the metals. Salts of thallium dialkyl, such as $TlMe_2Br$ and $TlEt_2Cl$, have been obtained by J. Meyer and Bertheim[1] from the action of organo-magnesium halides on thallic chloride according to the relation $TlCl_3 + 2MgRCl = TlR_2Cl + 2MgCl_2$. Magnesium methyl iodide reacts with phosphorus trichloride at $-20°$ to give tetramethyl-phosphonium chloride, and under varying conditions mono-, di-, and tri-substituted phosphines may be obtained; arsenic trichloride gives a product which, on oxidation, yields principally trialkylarsine oxide.[2]

Hydrocarbons.

The slow combustion of hydrocarbons at temperatures below their ignition points has been further studied by Bone and Stockings.[3] It had previously been shown[4] that the final products of oxidation of methane are carbon monoxide, carbon dioxide, and steam, and that formaldehyde is formed as an intermediate product. Neither free hydrogen nor free carbon is produced at any stage of the operation. The authors conclude that the oxidation of methane takes place in two successive stages, namely, the production of formaldehyde and steam, and the further rapid oxidation of formaldehyde to carbon monoxide, carbon dioxide, and steam. The observations have now been extended to ethane, and also to ethyl alcohol and acetaldehyde, and the principal conclusions arrived at may shortly be summarised as follows: under similar conditions, ethane burns much more rapidly than methane, and the oxidation takes place in both cases at temperatures much below that at which steam is appreciably formed from oxygen and hydrogen. When ethane reacts with less oxygen than is required to burn the whole of it to carbon monoxide and water, there is no preferential combustion either of hydrogen or carbon. The combustion proceeds in several well-defined stages, involving the formation of oxygenated compounds; acetaldehyde is shown to be produced in the first stage, and there is much probability that ethyl alcohol is really the primary product. In the second stage, formaldehyde, carbon monoxide, and steam result, and the formaldehyde finally undergoes further oxidation to carbon monoxide, carbon dioxide, and steam, formic acid being probably an intermediate product.

Hydrogen or methane, or both, may appear in the products due to the decomposition of the vapours of formaldehyde and acetaldehyde by heat and a little ethylene may result from the decomposition of

[1] *Ber.*, 1904, **37**, 2051.
[2] Auger and Billy, *Compt. rend.*, 1904, **139**, 597.
[3] *Trans.*, 1904, **85**, 693.
[4] Bone and Wheeler, *Trans.*, 1903, **83**, 1074.

ethane itself. Carbon is not liberated below the ignition points of the reacting mixtures, but if the temperature is allowed to rise to the ignition point an explosion occurs with the liberation of carbon and hydrogen, together with some acetylene and ethylene. Ethyl alcohol reacts with oxygen far more rapidly than ethane under similar conditions, and the operation involves, as in the case of ethane, the successive formation of acetaldehyde and of formaldehyde with carbon monoxide. In the case of acetaldehyde, it was shown that, in addition to formaldehyde, considerable quantities of methane and carbon monoxide are formed owing to the purely thermal decomposition of the acetaldehyde.

Although methyl alcohol could not be detected among the products of the slow combustion of methane, the authors have shown that, in the case of ethane, ethyl alcohol is formed. According to Armstrong's view,[1] the hydrocarbon in the initial stage of the operation merely undergoes hydroxylation, and when this has taken place further hydroxylation takes place more rapidly, so that the initial product may escape observation.

More recently,[2] Bone and Wheeler have extended these investigations to the study of ethylene, and their principal conclusions may be briefly stated as follows:

There is no preferential combustion of either carbon or hydrogen when ethylene reacts with oxygen in quantity insufficient to burn it completely. Formaldehyde is the most prominent intermediate oxidation product, and the formation of aldehydes precedes that of steam and oxides of carbon. There is no separation of carbon or liberation of acetylene, even in the explosive combustion of ethylene, except when the oxygen present is insufficient to burn the hydrocarbon to formaldehyde; under these conditions, the excess of ethylene is thermally decomposed, yielding carbon, hydrogen, methane, and traces of acetylene.

Henriet[3] has shown by a variety of reactions that formaldehyde is contained in ordinary atmospheric air, and he gives the proportion as 2 to 6 grams per 100 cubic metres. The quantity was estimated by passing the filtered air through U-tubes containing mercuric oxide and heated to 250°. In this way, the formaldehyde is oxidised to carbon dioxide, and this is absorbed in potash bulbs, allowance, of course, being made for the carbon dioxide originally present as such in the air. Gautier[4] points out that when air contains more than 0·5 to 1 gram of formaldehyde in 100 cubic metres it ceases to be respirable; Henriet consequently suggests that the large proportion which he found in normal air may have been present in some form of combination, such, for example, as methylal.

[1] *Proc. Roy. Soc.*, 1904, **4**, 86.
[2] *Trans.*, 1904, **85**, 1637.
[3] *Compt. rend.*, 1904, **138**, 203, 1272.
[4] *Ibid.*, **139**, 67.

Trillat[1] finds that various combustible substances, such as coal, peat, wood, cork, caoutchouc, and tobacco, when burnt in a glass tube in a current of air, give, in all cases, quantities of formaldehyde varying from 1/1000th to 1/100,000th of the weight of substance burnt. From these results, it is concluded that the formaldehyde found by Henriet in atmospheric air has its origin in processes of limited combustion of compounds containing carbon and hydrogen.

Alcohols.

Primary alcohols may be prepared from the corresponding amides by acting with metallic sodium on the amide dissolved in ethyl alcohol; on adding water and distilling in steam, a mixture of amine and primary alcohol passes over, which can be separated in the usual way by means of an acid. Bouveault and Blank[2] have in this way obtained *n*-hexyl alcohol from the amide of *n*-hexoic acid and benzylcarbinol from phenylacetic acid.[3]

For the preparation of tertiary alcohols by means of Grignard's reaction, the following additional method has recently been published by Grignard.[4] The magnesium alkyl halide RMgX is first acted on by dry carbon dioxide in ethereal solution, when, as the author has previously shown (1901), the additive compound $R\cdot CO_2\cdot MgX$ is formed. If, now, the excess of carbon dioxide is removed and the product is further acted on by a compound R′MgX, the following change takes place:

$$R\cdot CO_2\cdot MgX + 2R'MgX = O(MgX)_2 + CRR_2'\cdot OMgX\ ;$$

the latter compound on hydrolysis then yields the corresponding tertiary alcohol.

Diethyl*iso*amyl-, *iso*butyldi*iso*amyl-, and phenyldiethyl-carbinols were obtained in this way.

Although tertiary alcohols normally result from the action of Grignard's reagent on ketones, it was found that in the case of unsaturated ketones in which the double linking is situated near the carbonyl group the product of the reaction was an unsaturated hydrocarbon, since the tertiary alcohol became dehydrated during the process. Fallenberg[5] now finds, however, that in the cases of mesityl oxide and phorone it is possible to isolate the tertiary alcohols which are formed in the first stage, and that they can be distilled unchanged in a vacuum. Mesityl oxide, when acted upon by magnesium methyl iodide, gives a product which, when decomposed by dilute acetic acid, yields 2 : 4-dimethylpentene-(3)-ol-(2), $CMe_2{:}CH\cdot CMe_2\cdot OH$, which is a

[1] *Compt. rend.*, 1904, **138**, 1613. [2] *Ibid.*, 148.
[3] Compare also Guareschi, *Atti R. Accad. Sci. Torino*, 1904, **39**, 418. *Compt. rend.*, 1904, **138**, 152. [5] *Ber.*, 1904, **37**, 3578.

colourless liquid boiling at 46°/14 mm. When this tertiary alcohol is distilled under the ordinary pressure, it loses water, giving the dimethylpentadiene which Grignard obtained (1900) in a single stage. Phorone, when similarly treated, gives 2 : 4 : 6-trimethylheptadiene-(2 : 5)-ol-(4), $CMe{:}CH{\cdot}CMe(OH){\cdot}CH{:}CMe_2$.

This alcohol crystallises in long, white needles, which melt at 57·5°, and on repeatedly distilling it over sodium it yields a colourless liquid hydrocarbon, which proves to be trimethylheptatriene,

$$CMe_2{:}CH{\cdot}C(:CH_2){\cdot}CH{:}CMe_2.$$

For the characterisation and purification of certain alcohols, Bouveault[1] recommends the conversion of the alcohol into its pyruvic ester, and of this into its semicarbazone. Primary and secondary alcohols give in this way semicarbazones which are insoluble in water, but which crystallise well from organic solvents; from these compounds, the alcohols can be regenerated by the action of alcoholic potash. Tertiary alcohols are decomposed when boiled with pyruvic acid, yielding an ethylenic hydrocarbon and water.

Kling and Viard[2] suggest a method of distinguishing primary, secondary, and tertiary alcohols which is based on their different behaviour when heated. Tertiary alcohols become dehydrated at the temperature of boiling naphthalene (218°), whilst primary and secondary alcohols are unchanged. At the boiling point of anthracene (360°), both secondary and tertiary alcohols are decomposed, only primary alcohols remaining intact. These changes can be followed by determination of the vapour density at the temperatures mentioned.

Aldehydes and Ketones.

Several new methods have recently been published for the synthetical preparation of aldehydes. Tschitschibabin,[3] for example, finds that the esters of orthoformic acid react with organo-magnesium haloids to give acetals, and these, when hydrolysed with dilute sulphuric acid, yield the corresponding aldehydes,

$$CH(OEt)_3 + RMgI = CHR(OEt)_2 + EtO{\cdot}MgI.$$

Béhal and Sommelet[4] first prepare the ethers of α-glycols of the types $OH{\cdot}CR_2{\cdot}CH_2{\cdot}OX$ and $OH{\cdot}CRR_1{\cdot}CH_2{\cdot}OH$ (from ethyl ethoxyacetate, or from ketones of the type $R{\cdot}CO{\cdot}CH_2{\cdot}OEt$, by means of Grignard's reaction). These are then decomposed by heating with dry oxalic acid to 110—115°, when the corresponding substituted aldehydes are produced, the change proceeding probably as follows:

$$OH{\cdot}CR_2{\cdot}CH_2{\cdot}OX \longrightarrow CR_2{:}CH{\cdot}OX \longrightarrow CR_2{:}CH{\cdot}OH \longrightarrow CR_2H{\cdot}CHO.$$

[1] *Compt. rend.*, 1904, **138**, 984. [2] *Ibid.*, 1172.
[3] *Ber.*, 1904 **37** 186. [4] *Compt. rend.*, 1904, **138**, 89.

Blaise [1] shows that certain lactides on distillation give aldehydes in the following way: $CHR<^{CO\cdot O}_{O\cdot CO}>CHR = 2CO + 2RCHO$, a small proportion of an unsaturated acid being simultaneously formed. Starting from a fatty acid, say hexoic acid, he first obtains the α-monobromo-derivative, and from this the hydroxy-derivative, which on heating gives the lactide, and this on distillation the aldehyde as above. He is of opinion that the aldehyde results from the decomposition of the lactide and not of the hydroxy-acid itself. But Le Sueur, in an earlier communication,[2] has found that in the case of hydroxystearic acid the action of heat is to give carbon monoxide, formic acid, a lactide, and 50 to 60 per cent. of margaric aldehyde, $C_{16}H_{33}\cdot CHO$. Since this change can take place at a lower temperature than that at which the lactide is decomposed, he concludes that the aldehyde is formed directly from the acid and not from the lactide. Margaric aldehyde, obtained by Le Sueur in this way,[3] is a white solid melting at 35—36°, which slowly polymerises on keeping; on oxidation, it yields margaric acid, which is perhaps identical with the product obtained by Kraft, in 1879, from methyl heptadecyl ketone. Blaise (*loc. cit.*) recommends the above series of operations as a means of systematically degrading certain acids, and he has applied the method for the degradation of hexoic, pelargonic, lauric, myristic, and palmitic acids.

A method of producing aldehydes of the type CRR'H·CHO from ketones, which is said to be of general application, has recently been published by Darzens.[4] The ketone R·CO·R' is mixed with ethyl chloroacetate and acted upon by sodium ethoxide in the state of powder. The result is the formation of an unstable acid, which splits up into carbon dioxide and the aldehyde CRR'H·CHO.

It has been shown by Blank and Finkenbeiner and by Harden that when formaldehyde is acted on by hydrogen dioxide in alkaline solution the result is free hydrogen and a metallic formate. Geisow [5] now shows that if the action takes place in neutral or acid solution no formic acid is produced, but only carbon dioxide and free hydrogen. In these reactions, the hydrogen appears to come from the formaldehyde, and not from the hydrogen dioxide, since barium peroxide gives similar results. The peroxides of lead and manganese act on formaldehyde to give formates.

Cryoscopic determinations made by Litterscheid and Thimme [6] indicate that even in dilute aqueous solution formaldehyde exists partly in a polymerised form. Diformaldehyde, $C_2H_4O_2$, is said to

[1] *Compt. rend.*, 1904, **138**, 697.
[2] *Proc.*, 1904, **20**, 14.
[3] *Trans.*, 1904, **85**, 833.
[4] *Compt. rend.*, 1904, **139**, 1214.
[5] *Ber.* 1904, **37**, 515.
[6] *Annalen*, 1904, **334**, 1

separate in flakes when the vapour of formaldehyde is passed into chloroform at about 130°, the change being greatly increased by sunlight.[1]

By heating trioxymethylene with water, Seyewetz and Gibello[2] have obtained four polymerides of formaldehyde which differ in melting points and solubilities from the modifications already known (paraformaldehyde, its hydrate, trioxymethylene, and α-trioxymethylene). The molecular weights of these new modifications is said to approximate to 60 in the freshly prepared solutions, whilst the vapour density in each case indicated the number 30. The same two authors[3] have found that the condensation of trioxymethylene to a mixture of sugars is easily brought about by means of sodium sulphite, the change taking place much more readily than the corresponding condensation of formaldehyde by bases. The nature of the resulting sugars depends somewhat on the proportions and on the conditions of the experiment; from the action of phenylhydrazine on the resulting mixtures, they were able to identify formosazone, glycerosazone, and, under certain conditions, α-acrosazone.

Hydracrylic aldehyde, $CH_2(OH)\cdot CH_2\cdot CHO$, has been obtained by Nef[4] as a colourless oil boiling at 90° under 18 mm. pressure; it is prepared by heating acrolein with four times its weight of water at 100° for about 20 hours. It is very easily soluble in water, but dissolves only very slightly in ether; heating with potassium hydrogen sulphate reconverts it into acrolein, and by the action of dilute alkalis it gives rise to crotonaldehyde. The semicarbazone is crystalline and melts at 114°.

r-Lactic aldehyde, $CH_3\cdot CH(OH)\cdot CHO$, appears to be incapable of existing in the isolated form, but was obtained[5] as acetate by the action of silver acetate on α-iodopropaldehyde. This acetate is a dark oil having an aromatic odour, which boils at 55—65° under 19 mm. pressure and gives a crystalline semicarbazone. When heated with water, it yields acetol and acetic acid (see page 68).

Lapworth in the course of an extensive study on the addition of hydrogen cyanide to carbon compounds has recently shown[6] that the addition is usually much more easily accomplished when potassium cyanide is present; carbonyl compounds can, in fact, in many cases actually remove hydrogen cyanide from an alkaline solution of potassium cyanide. In a more recent communication,[7] this author describes the results of the action of potassium cyanide on mesityl oxide. It is shown that the initial product is mesitononitrile, and this, on prolonged

[1] Körber, *Pharm. Zeit.*, 1904, **49**, 608.
[2] *Compt. rend.*, 1904, **138**, 1225.
[3] *Bull. Soc. chim.*, 1904, [iii], **31**, 434.
[4] *Annalen*, 1904, **335**, 219.
[5] *Loc. cit.*, p. 266.
[6] *Trans.*, 1903, **83**, 995.
[7] *Ibid.*, 1904, **85**, 1214.

heating, is hydrolysed by the resulting potassium hydroxide, yielding mesitonic acid,

$$C(CH_3)_2{:}CH{\cdot}CO{\cdot}CH_3 + KC \quad + 2H_2O = CO_2K{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + NH_3.$$

In one operation, therefore, it is possible in this way to synthesise a γ-ketonic acid from an $\alpha\beta$-unsaturated ketone.

Carbohydrates.

Bertrand [1] gives a complete historical account of the chemistry of *sorbose* and *sorbitol* together with a concise summary of his remarkable work on the oxidation of various polyhydric alcohols and sugars by the agency of the "sorbose bacterium." In the latter organism, it is pointed out, we have the equivalent of a powerful chemical agent by whose assistance it is possible to prepare many new compounds and to gain much knowledge with regard to the constitution of various carbohydrates and allied substances. In the case of polyhydric alcohols, the effect of its action is to bring about the oxidation of a $-CH{\cdot}OH$ group to $:CO$, and consequently the formation of a ketose; in this way, the ketoses—dihydroxyacetone, erythrulose, arabinulose, sorbose, lævulose, perseulose, and volemulose—were obtained from the respective polyhydric alcohols—glycerol, erythritol, arabitol, sorbitol, mannitol, perseitol, and volemitol. Glycol, *l*-xylitol, and *d*-dulcitol are not attacked, their immunity being evidently conditioned by stereochemical structure; according to the author's view, a $-CH{\cdot}OH$ group is only open to attack by the organism when its hydroxyl group is not adjacent to a hydrogen atom on the same side in the configuration formula.

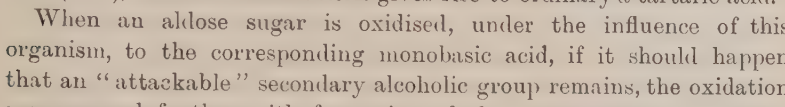
In the case of reducing sugars, it is found that all are attacked; aldoses are oxidised quantitatively to the corresponding monobasic acids, whereas ketoses are only slowly altered and give no characteristic products.

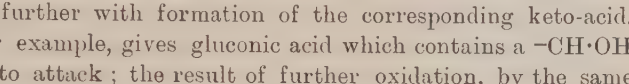
Amongst this author's most recent observations which are described in this paper may be mentioned the reduction, by sodium amalgam, of sorbose to a mixture of *d*-sorbitol and *d*-iditol. The properties of *dihydroxyacetone*, which is easily obtained by the above-mentioned method, have also been more completely studied, and it is shown that, contrary to previous statements, this carbohydrate is capable of undergoing alcoholic fermentation with yeast, although with difficulty. From one gram of dihydroxyacetone, the yield of alcohol amounted, after 10 days, to 15—125 milligrams, according to the kind of yeast employed. As already mentioned, ordinary erythritol yields the corresponding ketose, erythrulose; the latter, when reduced by sodium

[1] *Ann. Chim. Phys.*, 1904, [viii], **3**, 181.

amalgam gives rise to two tetritols; one of these is ordinary *l*-erythritol and the other is the hitherto unknown d-*erythritol*, which is the optical antipode of the product which Maquenne previously obtained (1901) from xylose by degradation and reduction. On oxidation with nitric acid (1 : 2), this new modification gives rise to ordinary *d*-tartaric acid.

When an aldose sugar is oxidised, under the influence of this organism, to the corresponding monobasic acid, if it should happen that an "attackable" secondary alcoholic group remains, the oxidation may proceed further with formation of the corresponding keto-acid. *d*-Glucose, for example, gives gluconic acid which contains a $-CH\cdot OH$ group liable to attack; the result of further oxidation, by the same agency, is "*oxygluconic*" *acid*.





The latter acid appears to be identical in every way with that which Boutroux, in 1888, prepared also by the fermentation of glucose; in this case, however, the active ferment was lost, and in consequence the acid had been but little studied.

It was formerly supposed that only primary hydrazines were capable of producing osazones from aldoses or ketoses, the reaction involving oxidation of the $CH\cdot OH$ or $CH_2\cdot OH$ group adjacent to the CO group. But Neuberg, in 1902, showed that phenylmethylhydrazine can give an osazone by direct action on lævulose and on some other ketoses, and it appeared, in the first instance, that this behaviour was limited to ketoses and to osones. Ofner now states[1] that *d*-glucose can react directly with phenylmethylhydrazine to give an osazone identical with that which Neuberg obtained from lævulose and Fischer from glucosone. But Neuberg[2] points out that if the conditions which he recommended are followed the distinction is still valid. With regard to the action of unsymmetrical secondary aromatic hydrazines such as phenylbenzylhydrazine, it would appear that these can react with the phenylhydrazones of aldoses to give osazones, but not with the sugars themselves. Pure phenylbenzylhydrazine is, in fact, said to be without action on either dextrose or lævulose, and the product previously obtained by Neuberg from lævulose, and supposed to be *d*-fructosephenylbenzylosazone, is now shown to be a mixture of phenylosazone and phenylbenzylosazone, and is only produced when

[1] *Ber.*, 1904, **37**, 3362. [2] *Ibid.*, p. 4616.

the phenylbenzylhydrazine contains phenylhydrazine. In this connection, it may be of interest to mention a recent observation of the writer that glycollic aldehyde readily reacts with phenylbenzylhydrazine to give the phenylbenzylosazone of glyoxal.[1]

Many acid hydrazides, such as *p*-bromobenzoylhydrazide, react with aldoses to give hydrazones which are insoluble or sparingly soluble in most solvents. From these compounds, the original sugars are easily regenerated by the action of dilute sulphuric acid, benzaldehyde, or pyridine. It is stated that ketoses do not give hydrazones by this treatment.[2]

In order to distinguish aldoses from ketoses, Berg [3] proposes a method based on the fact that the former are readily oxidised by bromine water to the corresponding hydroxy-acids, and that the latter give an intense yellow colour with ferric chloride. The sugar to be examined is heated for 10 minutes with bromine water to 60—70°, the excess of bromine expelled, and the product tested with ferric chloride and a drop of hydrochloric acid. The aldoses examined—glucose, galactose, arabinose, and xylose—all gave an intense yellow colour when submitted to this treatment, whereas lævulose and sorbose gave no colour.

It has been shown by the writer [4] that ketohexoses and substances which yield them by hydrolysis, when oxidised in presence of iron by hydrogen peroxide, or by chlorine, at 80—90°, yield a product which, when heated with phenylhydrazine-*p*-sulphonic acid, gives a brownish-pink dye-stuff. This reaction appears to be very characteristic of ketohexoses; the aldoses are only very slowly oxidised under similar conditions and the lower sugars do not give a similar colour with the hydrazine compound.

For the purpose of separating and identifying the constituents of a mixture of certain sugars, Votoček and Vondráček [5] recommend a process of successive treatment with different hydrazines, such as phenyl-, phenylmethyl-, and diphenyl-hydrazines. The strength of the solution is adjusted so as to contain about 5 per cent. of the reducing sugars, and an equivalent quantity of a suitable hydrazine is added in the form of acetate. The resulting hydrazone is filtered off and the filtrate is treated with a second hydrazine, which causes the separation of another sugar as hydrazone or osazone, and these operations may be continued even for a third sugar.

Mannose and galactose, for example, can be separated by first precipitating the mannose as phenylhydrazone, and, secondly, the galactose

[1] Compare Ruff and Ollendorff, *Ber.*, 1900, **33**, 1806.
[2] Kahl, *Zeit. Ver. Deut. Zuckerind.*, 1904, **584**, 1091.
[3] *Bull. Soc. chim.*, 1904, [iii], **31**, 1216.
[4] *Brit. Assoc. Report*, 1904. [5] *Ber.*, 1904, **37** 3854.

as phenylmethylhydrazone. A mixture of galactose and glucose is similarly identified by acting successively with phenylmethylhydrazine and phenylhydrazine, which give the corresponding hydrazone and osazone respectively.

Morrell and Bellars[1] have continued their investigations on the formation of osones from hexoses, pentoses, and bioses by the general method of oxidation with hydrogen peroxide in presence of ferrous iron and have traced a connection between the diminution of optical activity, change in reducing power, acidity, and yield of osazone during oxidation. They show that glucose, fructose, galactose, arabinose, rhamnose, and maltose give crystalline compounds with guanidine; these compounds form strongly alkaline aqueous solutions from which the guanidine can be completely removed by acids.

By keeping milk-sugar for some time in contact with calcium hydroxide, *iso*saccharin and metasaccharin were obtained by Cuisinier and by Kiliani respectively (1882—1883); Kiliani and Loeffler[2] now find that parasaccharin is also produced in considerable quantity. When the latter substance is oxidised by hydrogen peroxide in presence of iron, "degradation" occurs with formation of parasaccharopentose, $C_5H_{10}O_4$. This is a crystalline substance which reacts with phenylbenzylhydrazine to form a hydrazone, and has the constitution

$$CH_2(OH)\cdot CH_2\cdot CO\cdot CH(OH)\cdot CH_2\cdot OH.$$

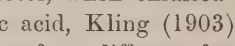
From this, it is concluded that parasaccharic acid must have the formula $CH_2(OH)\cdot CH_2\cdot C(CO_2H)(OH)\cdot CH(OH)\cdot CH_2\cdot OH$. By oxidising the barium salt of the latter acid with strong nitric acid (sp. gr. 1·39), an easily soluble crystalline acid is obtained, which proves to be hydroxycitric acid, $C_6H_8O_8,H_2O$; this has hitherto been but little known and only scantily described. It is tribasic and gives characteristic copper and dipotassium salts. These authors point out that the modifications of saccharic acid may conveniently be identified by means of their crystalline quinine salts.

The action of calcium hydroxide on *l*-arabinose gave rise to considerable quantities of calcium lactate, and, in addition, salts having the composition $Ca(C_5H_9O_5)_2$ and $Ca(C_6H_{11}O_6)_2$ were obtained. The formation of a six-carbon acid from a five-carbon sugar is explained by supposing that part of the sugar first breaks down into simpler parts, which then unite to build up synthetically the more complex molecule.[3]

It would appear that *acetol* should appropriately be considered in connection with the family of the carbohydrates, since it may be regarded as the methyl derivative of the first sugar or methyldiose. Nef, in a highly interesting course of researches on the dissociation of compounds

[1] *Brit. Assoc. Report*, 1904.
[2] *Ber.*, 1904, **37**, 1196 and 3612.
[3] Kiliani and Koehler, *loc. cit.*, p. 1210.

belonging to the glycol or glycerol series,[1] has made a careful study of the formation, properties, and relationships of acetol. He shows that it is produced, amongst other substances, when glycerol is slowly led through a tube which is filled with pumice and heated to 430—450°. It is also formed when α-bromopropionaldehyde is heated with potassium acetate or formate. Further, he finds that, when α-iodopropionaldehyde is heated with silver acetate, a product is obtained which he identifies as the acetate of *r*-lactic aldehyde. When this acetate is heated with water to 100°, it yields acetol and acetic acid. In view of these facts, the question arises whether acetol and lactic aldehyde may not be identical or tautomeric. It is shown, however, that on heating acetol with acetic anhydride only acetol acetate is produced quite free from the acetate of lactic aldehyde, the two acetates being readily distinguished by their semicarbazones ; the acetol compound melts at 145°, and that of lactic aldehyde at 163°. This author arrives at the conclusion that acetol is identical with hydroxyacetone and that the isomeric lactic aldehyde cannot exist in the isolated condition, but becomes transformed into acetol.

Owing to the observation that acetol, when oxidised with alkaline cupric oxide, gives rise to lactic acid, Kling (1903) considered that, in solution, acetol exists partly in a form different from hydroxyacetone, and suggested the possibility of the group  He has later[2] attacked this question by means of Grignard's reaction, since it had been shown by Grignard that compounds containing this group, when acted upon by organo-magnesium halides at low temperatures, give secondary alcohols of the type $OH{\cdot}CHR{\cdot}CH_2X$, whereas tertiary alcohols are produced from compounds in which the $-CO-$ group is present. The behaviour of acetol and its esters towards this reagent is found to be that of a ketonic compound, tertiary alcohols, or their derivatives, being obtained.

The action of dilute acids on cellulose causes under certain conditions, a destruction of the tenacity of the fibre, and the resulting powder has been called " hydrocellulose," the formula assigned to it being $C_{12}H_{22}O_{11}$ (Girard, 1875—1881). Stern[3] has recently examined the behaviour of flax and cotton cellulose when boiled with 5 per cent. sulphuric acid, and finds that instead of a gain in weight there is always a loss, and a certain amount of soluble matter is also formed of which a portion appears to be *d*-glucose. The friable mass remaining is shown by analysis to have the same composition as the original

[1] *Annalen*, 1904, **335**, 191—333. [2] *Compt. rend.*, 1903, **137**, 756.
[3] *Trans.*, 1904, **85**, 336.

cellulose. The author concludes that hydrocellulose is not formed, and that the only essential change, apart from the disintegration, is that a portion of the cellulose becomes hydrolysed into soluble products.

Cross and Bevan, however, consider that these differences are due to the fact that the conditions of Stern's experiments are not altogether the same as those employed by Girard, and they propose to retain the name of hydrocellulose for the products of the action of acids on cellulose. These, they say, are certainly hydrolysed, although in many cases they may have the same composition as the parent substance.

Knecht[1] shows that when cellulose is treated with nitric acid of sp. gr. 1·415 a "labile" nitrate having the composition $C_6H_{10}O_5,HNO_3$ is obtained. When this is decomposed by water, a product free from nitric acid results, which contains 4 per cent. more water than the original cellulose, and appears to be a hydrate. The process is therefore quite analogous to the mercerisation of cotton by alkalis; in this case, the compound $(C_6H_{10}O_5)_2,Na_2O$ is probably first formed, and this is decomposed by water, forming sodium hydroxide and a cellulose hydrate, $(C_6H_{10}O_5)_2,H_2O$.

It is customary to assume that the molecular formula for cellulose must be represented by a multiple of the empirical formula, the double value $C_{12}H_{20}O_{10}$ being often regarded as the minimum. The reasons usually advanced in favour of this assumption, such as the insoluble and colloidal nature of cellulose and the existence of a pentanitrate, are considered by Green[2] to be altogether insufficient and, until further definite experimental evidence is forthcoming, he prefers to employ the single formula $C_6H_{10}O_5$. He shows, further, that no satisfactory constitutional formula has yet been proposed which gives an adequate indication of the chemical behaviour of cellulose, and suggests that it might be regarded as an inner anhydride of glucose having the constitution

$$\begin{array}{l} CH(OH)\cdot CH\cdot CH\cdot OH \\ | \qquad\quad >O >O \\ CH(OH)\cdot CH\cdot CH_2 \end{array} .$$

This formula would account for a large number of important facts, among which the following may be mentioned.

(*a*) That the highest nitrate (assuming the C_6 formula) is the trinitrate; (*b*) that the absence of a carbonyl group is indicated by the behaviour of phenylhydrazine and hydroxylamine; (*c*) that ω-bromomethylfurfural results by the action of dry hydrogen bromide; (*d*) the production of *iso*saccharic and dihydroxybutyric acids by the action of milk of lime on oxycellulose, and (*e*) the formation of hydroxypyruvic acid when cellulose nitrate is heated with dilute sodium hydroxide.

[1] *Ber.*, 1904, **37**, 549. [2] *Zeit. Farb. Text. Ind.*, 1904, **3**, 97.

Several objections to this formula are raised by Cross and Bevan [1] and are answered by Green.[2] The objection that the formula does not indicate the possibility of a tetra-acetate would appear to be disposed of, since a determination of the acetyl groups in this supposed tetra-acetate by Perkin's method proves it, in reality, to be a triacetate.[3]

Skraup and König, in 1901, obtained a biose, $C_{12}H_{22}O_{11}$, from cellulose by treatment with acetic anhydride and sulphuric acid, and decomposition of the resulting octoacetylcellulose with alcoholic potash. This sugar (cellose) has been further examined by Maquenne and Goodwin.[4] With hydroxylamine, it reacts to give a viscous oxime, and by action of carbanil it is converted into a hexaphenylurethane, $C_{12}H_{20}O_{10}(CON{\cdot}C_6H_5)_6$, which appears therefore to be derived from an anhydride containing only six hydroxyl groups. When oxidised by bromine in presence of water, cellose gives, as an uncrystallisable syrup, "cellobionic acid," $C_{12}H_{22}O_{12}$, which reduces Fehling's solution only after hydrolysis; this direct formation of a corresponding monobasic acid on oxidation proves the presence of an aldose group in the molecule of cellose.

These authors have also examined [5] the action of carbanil (phenylcarbimide) on various other sugars, such as arabinose, xylose, dextrose, and lactose; they find in every case that each hydroxyl group is replaced by the carbamate residue. They show also [6] that the semicarbazones of many of the sugars are easily obtained, but they are not very well suited for the identification of the latter, since the melting points are not sharply defined.

From results obtained by the cryoscopic method, Sabanéeff, in 1890, estimated the molecular weight of glycogen to be about 1620, corresponding to the formula $(C_6H_{10}O_5)_{10}$. Similar determinations have recently been made, using improved modern apparatus, by Mme. Gatin-Gružewska, who comes to the conclusion that either the previous result is far too low or that the substance is insoluble, and its molecular weight cannot be determined. The numbers actually obtained by the author would point to a molecular weight of 140,000.

Acids and Esters.

A method for the characterisation of fatty acids has been suggested by Locquin,[7] which consists in converting them into the corresponding

[1] *Zeit. Farb. Text. Ind.*, 1904, **3**, 197. [2] *Ibid.*, p. 309.

[3] Cross and Bevan, however, still consider that the evidence is not conclusive and suggest that a fourth acetyl group may be present which behaves differently to the other three. *Zeit. Farb. Text. Ind.*, 1904, **3**, 441.

[4] *Bull. Soc. chim.*, 1904, [iii], **31**, 854. [5] *Compt. rend.*, 1904, **138**, 633.

[6] *Bull. Soc. chim.*, 1904, [iii], **31**, 1075. [7] *Compt. rend.*, 1904, **138**, 1274.

hydroxyacetone esters by the action of chloroacetone upon the sodium salts :

$$R{\cdot}CO{\cdot}ONa + CH_2Cl{\cdot}CO{\cdot}CH_3 = R{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + NaCl.$$

These esters can then be readily identified by means of their semicarbazones, which are easily purified and have sharply-defined melting points.

As an example of one of the ways in which Grignard's reaction may be employed in the synthesis of acids may be mentioned the simple formation of pivalic (trimethylacetic) acid from *tert.*-butyl chloride.[1] The additive compound which is formed by the action of magnesium is, in this case, acted on by dry carbon dioxide in ether solution, when a 30 per cent. yield of pivalic acid is obtained on hydrolysis. *tert.*-Amyl chloride similarly gives a 60 per cent. yield of $\alpha\alpha$-dimethylbutyric acid :

$$R_3C{\cdot}MgCl \longrightarrow R_3C{\cdot}CO_2{\cdot}MgCl \longrightarrow R_3C{\cdot}CO_2H.$$

An isomeride of oleic acid has been obtained by Ponzio[2] from α-bromostearic acid ; the latter was first converted into the corresponding iodostearic acid (by the action of alcoholic potassium iodide), and this was then decomposed by alcoholic potash. The formula $CH_3(CH_2)_{14}{\cdot}CH{:}CH{\cdot}CO_2H$ is assigned by the author to this acid, which, on potash fusion, yields palmitic and acetic acids.

By the action of alcoholic potash on α-bromostearic acid, Le Sueur[3] obtains, together with α-hydroxystearic acid, an isomeride of oleic acid having the above constitution, which he designates as Δ^{α}-oleic acid. On oxidation with potassium permanganate, it yields first a dihydroxystearic acid, and, on further oxidation, palmitic acid.

Pimelic acid, which has hitherto only been obtained synthetically by a comparatively tedious method, can be readily prepared from 1 : 5-di-iodo- or dibromo-pentane ; by action of potassium cyanide, the corresponding nitrile is obtained, and this, on saponification by hydrochloric acid, gives a theoretical yield of pimelic acid :

$$Br{\cdot}[CH_2]_5{\cdot}Br \longrightarrow NC{\cdot}[CH_2]_5{\cdot}CN \longrightarrow CO_2H{\cdot}[CH_2]_5{\cdot}CO_2H.$$

Hamonet[4] and Braun[5] have both obtained this result, working only on somewhat different lines. The latter starts with benzoylpiperidine, which, by the action of phosphorus pentachloride (or pentabromide), is converted into a mixture of benzonitrile and $\alpha\epsilon$-dichloropentane, and this mixture may be used directly for the above

[1] Bouveault, *Compt. rend.*, 1904, **138**, 1108.
[2] *Atti R. Accad. Sci. Torino*, 1904, **39**, 552.
[3] *Trans.*, 1904, **85**, 1708.
[4] *Compt. rend.*, 1904, **139**, 59. [5] *Ber.*, 1904, **37**, 3588.

synthesis, since the benzonitrile is easily removed by steam distillation.

With the exception of the tartaric acids, our knowledge of the dihydroxy-derivatives of acids of the succinic series has hitherto been somewhat limited, and an interesting communication has recently been published by Rosenlew[1] on the *βε-dihydroxyadipic acids*. Two isomeric βε-dibromoadipic acids were prepared by Aschan's method, and these, by the action of baryta water, were converted into the corresponding dihydroxy-acids. These two acids melt at 173° and 132° respectively, and are designated as the A- and B-forms. The A-acid, which is the more soluble, appears to be the externally compensated or racemic form, and the B-acid the internally compensated form.

Considerable attention has of late been paid to the alkyl derivatives of barbituric acid owing to their medicinal value as hypnotics. Fischer and Dilthey[2] find that when urea is acted upon by diethylmalonic acid in presence of phosphorus oxychloride, the result is not diethylbarbituric acid, as might have been expected from the previous investigations of Thorne and of Grimaux; instead of this, a ureide of diethylacetic acid is obtained. But if, on the other hand, the condensation of the ester is effected with the agency of sodium ethoxide, the dialkylbarbituric acids can advantageously be prepared:

$$Et_2{:}C{:}(CO_2Et)_2 + (NH_2)_2CO + NaOEt = \begin{matrix} Et_2C\text{—}CO\cdot NNa \\ | \quad\quad | \\ CO\cdot NH\cdot CO \end{matrix} + 3EtOH.$$

The monoalkyl derivatives can similarly be obtained from the monoalkylmalonic esters.

Thiocarbamide, guanidine, and monoalkylcarbamides behave similarly to carbamides, but the *s*-dialkylcarbamides do not. Dialkylbarbituric acids can be obtained by the action of carbamide on dialkylmalonyl chlorides.

For the preparation of methyl esters of certain acids, Werner and Seybold[3] recommend the interaction of dimethyl sulphate with the alkali metal salt of the acid. It is shown that this method (which had previously been employed in special cases by H. Meyer, H. von Liebig, and others) is sometimes successful where the usual method of esterification with methyl alcohol cannot be applied.

In preparing esters by the action of sulphuric acid and alcohol, H. Meyer[4] recommends that the acid should be dissolved in concen-

[1] *Ber.*, 1904, **37**, 2090.
[2] *Annalen*, 1904, **335**, 334.
[3] *Ber.*, 1904, **37**, 3658.
[4] *Monatsh.*, 1904, **23**, 840.

trated sulphuric acid and an equivalent quantity of the alcohol added; the mixture is then poured on to crystallised sodium carbonate.

As an example of one of the typical reactions of Grignard's reagent on esters may be mentioned the recent work of Pogorželski,[1] who shows that when ethyl succinate is acted on by magnesium methyl iodide, the glycol, $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, can be obtained, the final result therefore consisting in the replacement of $\cdot CO_2Et$ by $\cdot CMe_2{\cdot}OH$.[2] Previously this glycol had been prepared by Zelinsky (1902) from acetonylacetone, also by the action of magnesium methyl iodide, the final change in this case being represented by the replacement of the :CO groups by $\cdot C(OH)Me$ in the usual way.

The esters of hydroxy-acids behave in a similar way; thus Frankland and Twiss[3] have recently shown that by the action of magnesium phenyl bromide on dimethyl tartrate a product is obtained which, after hydrolysis with dilute sulphuric acid, yields a tetraphenylerythritol, $OH{\cdot}C(C_6H_5)_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}C(C_6H_5)_2{\cdot}OH$, a compound which is isomeric with benzoinpinacone,

$$OH{\cdot}CH(C_6H_5){\cdot}C(C_6H_5)(OH){\cdot}C(C_6H_5)(OH){\cdot}CH(C_6H_5){\cdot}OH.$$

A further study has recently been made by Collie[4] of methyl fluoride, a compound first obtained by him in 1889 by the action of heat on tetramethylammonium fluoride. On subjecting this gas to the electric spark in a glass tube over mercury, it is almost immediately decomposed into carbon, hydrogen, and hydrogen fluoride,

$$4CH_3F = 4C + 4H_2 + 2H_2F_2.$$

On continued sparking, a filament begins to grow from the negative electrode, finally bridging the gap to the positive electrode. This filament proves to be pure silicon, evidently derived from the glass. Silicon fluoride is probably first formed, and is then reduced by the hydrogen.

It has been shown by Willstätter and Pummerer[5] that ethyl acetonedioxalate (which was obtained by Claisen in 1891 from acetone and ethyl oxalate by action of sodium ethoxide) can exist in two desmotropic forms. One of these melts at 104°, is colourless, has no dyeing properties, and appears to be the monoenolic form:

$$CO_2Et{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_2{\cdot}CO{\cdot}CO_2Et \text{ or}$$
$$CO_2Et{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Et.$$

The second modification, which can be obtained from the first by

[1] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 882.

[2] Compare also the reactions involved in the synthesis of terpineol by W. H. Perkin, jun., this vol., p. 117.

[3] *Trans.*, 1904, **85**, 1666. [4] *Ibid.*, 1318. [5] *Ber.* 1904, **37**, 3733.

the action of alkalis, melts at 98°, is lemon-yellow, and dyes wool a deep yellow colour. It is apparently the di-enolic form :

$$CO_2Et\cdot C(OH){:}CH\cdot CO\cdot CH{:}C(OH)\cdot CO_2Et.$$

The latter compound is of particular interest, since it appears to be the only known nitrogen-free member of the aliphatic series which acts as a dye-stuff.

Bases.

For the characterisation and estimation of amines, Sudborough and Hibbert[1] propose to make use of Grignard's reagent. Meunier[2] showed that with primary and secondary amines the reagent behaves in the following way :

$$RNH_2 + CH_3\cdot MgI = RNH\cdot MgI + CH_4 \text{ and}$$
$$RR_1NH + CH_3MgI = RR_1N\cdot MgI + CH_4.$$

The first-named authors find that this reaction with primary amines takes place quantitatively in the cold, but that on heating a second molecule of methane is liberated, probably according to the equation :

$$RNH\cdot MgI + CH_3\cdot MgI = RN(MgI)_2 + CH_4.$$

In the case of secondary amines, however, one molecule of methane is given for each molecule of amine, even on heating, and with tertiary amines no gas is evolved.

Cadaverine or pentamethylenediamine was synthetically prepared by Ladenburg in 1883—1886 by the reduction of trimethylene cyanide. A new synthesis of this base has now been effected by Braun[3] in the following way : $\alpha\epsilon$-dichloropentane is first prepared from piperidine in the manner indicated on p. 71, and in order to replace the halogen atoms by the amino-group, since the simple action of ammonia does not give good results in this case, the method of Gabriel was employed. This consists in acting on the halogen compound with the potassium derivative of phthalimide, and decomposing the resulting compound with hydrochloric acid. The changes involved are indicated in the following scheme :

$$C_5H_{10}{:}NH \longrightarrow C_5H_{10}N\cdot CO\cdot C_6H_5 \longrightarrow Cl(CH_2)_5Cl \longrightarrow$$
$$C_6H_4\langle{}^{CO}_{CO}\rangle N\cdot[CH_2]_5\cdot N\langle{}^{CO}_{CO}\rangle C_6H_4 \longrightarrow NH_2\cdot[CH_2]_5\cdot NH_2.$$

The cadaverine is at once obtained, in the form of its sparingly soluble hydrochloride, in a pure state, and the yield of the free

[1] *Proc.*, 1904, **20**, 165. [2] *Compt. rend.*, 1903, **136**, 758.
[3] *Ber.*, 1904, **37**, 3583.

base amounts to about 50 per cent. of the weight of piperidine employed.

Serine and *iso*serine, which are the α-amino-β-hydroxy- and β amino-α-hydroxy-derivatives, respectively, of propionic acid, were synthetically prepared in 1902 by Fischer and Leuchs; serine was obtained from glycollic aldehyde-ammonia and hydrogen cyanide, and *iso*serine from β-chlorolactic acid and ammonia.

*iso*Serine has now been synthesised in a different way by Ellinger,[1] and by Neuberg and Silbermann.[2] The method employed consists in acting on the monohydrobromide of $\alpha\beta$-diaminopropionic acid in aqueous solution with silver nitrite, the mixture being kept at about 40° for 3 or 4 days. The principal change may be represented as follows:

$$NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,HBr + AgNO_2 = NH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H + AgBr + N_2 + H_2O.$$

The two modifications of serine can be distinguished, as previously shown, by their phenylcarbimides, copper salts, and behaviour with naphthalene-β-sulphonic chloride.

The syntheses of cystein and of cystine have recently been accomplished by E. Erlenmeyer, jun.,[3] and it is shown that their constitution is to be represented by the formulæ $CH_2(SH){\cdot}CH(NH_2){\cdot}CO_2H$ and $[-S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_2$ respectively. When the ethyl ester of benzoylserine, $OH{\cdot}CH_2{\cdot}CH[NH(CO{\cdot}C_6H_5)]{\cdot}CO_2H$, is acted on by phosphorus pentasulphide, the hydroxylic oxygen is replaced by sulphur, giving the ester of benzoylcystein; this, on hydrolysis, yields cystein, and by oxidation of the latter, cystine is obtained.

A new synthesis of r-*leucine* (r-α-amino*iso*hexoic acid) is described by Bouveault and Locquin.[4] It is effected by the reduction of ethyl α-oximino*iso*butylacetate, $(CH_3)_2CH{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$, with aluminium amalgam in presence of ether. Leucinimide, which is the corresponding diketopiperazine derivative (see p. 77), is obtained by spontaneous decomposition of the ethyl ester.

An isomeride of leucine, which is described as *d-iso*leucine, has been obtained by Ehrlich[5] from the liquors to which the strontia-process has been applied in the manufacture of beet-root sugar. This author is of opinion that this isomeride nearly always occurs together with *l*-leucine as a primary product in the hydrolysis of proteids. The fact that these two forms of leucine can give mixed crystals probably explains the difficulty which is sometimes experienced in isolating

[1] *Ber.*, 1904, **37**, 335. [2] *Ibid.*, p. 341. [3] *Annalen*, 1904, **337**, 236.
[4] *Bull. Soc. chim.*, 1904, [iii], **31**, 1180.
[5] *Zeit. Ver. Deut. Zuckerind.*, 1903, **571**, 809, and *Ber.*, 1904, **37**, 1809.

ordinary *l*-leucine. The constitution of *d-iso*leucine is not fully established, but it appears not improbable that it is the β-amino-acid.

Polypeptides.

With the object of throwing further light on the nature of proteid substances, chemists have for some considerable time made attempts to obtain condensation products from those amino-acids—such as glycine, leucine, and asparagine—which result from the hydrolytic decomposition of proteids. As examples of some of the earlier attempts in this direction, one may refer to the formation of the so-called poly-aspartic anhydrides from asparagine and aspartic acid by Schaal (1871) and Schiff (1898), and the condensation of one of these anhydrides by Grimaux (1882). The product obtained in the latter case was a colloidal, gummy mass, which had many of the characters of a proteid and gave the "biuret reaction" with alkaline cupric oxide. Schutzenberger (1888—1891) also prepared proteid-like substances by heating amino-acids with urea and phosphoric oxide. Lilienfeld (1894) acted on ethyl glycine with condensing agents, such as potassium hydrogen sulphate or formaldehyde, and obtained a base which he called "biuret dimethylene," which had the percentage composition of gelatin, and which, when condensed with the esters of other amino-acids, gave products which exhibited some of the characters of proteids. But all of the above-mentioned products were amorphous, of unknown constitution, and generally difficult to identify as single substances. It is to Curtius and to Fischer—with the co-operation of their colleagues—that we are indebted for the systematic building up of complex compounds, the constitution of which is beyond doubt, from amino-acids in such a manner that the residues of these acids are coupled together, link by link, into "chains."

Such compounds may be regarded as being formed by the interaction of the amino-group of one acid with the carboxylic hydroxyl of the next, a molecule of water being eliminated :

$$NH_2 \cdot R'' \cdot CO \cdot OH \quad H \cdot NH \cdot R'' \cdot CO_2H.$$

The names glycyl, leucyl, alanyl, and so on, are given by Fischer to these $NH_2 \cdot R'' \cdot CO$ groups, which replace the hydrogen atom of the next NH_2 group, and the complex chains so produced are called by him "polypeptides."

In order to bring about this systematic linking, many entirely different methods have been devised. Curtius, in 1881, by the action of silver glycine on benzoyl chloride, obtained, in addition to other products, hippurylglycine, that is, the benzoyl derivative of glycyl-glycine, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, and two years later

he showed that the ethyl ester of glycine undergoes spontaneous decomposition, giving glycine anhydride and the so-called "biuret base." He showed later that this glycine anhydride has the bimolecular formula, and its reactions indicate that its constitution is to be represented as

$$\begin{matrix} NH\cdot CH_2\cdot CO \\ | \qquad\quad | \\ CO\cdot CH_2\cdot NH \end{matrix}$$

or diketopiperazine.

Fischer, in 1901, used this substance as the starting-point of his researches in the direction above indicated, and showed that when it was heated for a short time with concentrated hydrochloric acid the piperazine ring was broken and the hydrochloride of an amino-acid was obtained. This amino-acid is in fact glycylglycine,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

the simplest example of a dipeptide. The ester of this dipeptide reacts with ethyl chlorocarbonate, in presence of alkalis, to form the carbethoxy-derivative, $EtO\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$.

By introduction of the carbethoxy-group in this way, the very reactive amino-group is rendered more stable, and the ester of the resulting compound can now be made to condense with the esters of other amino-acids by simple heating. In this way, Fischer obtained the carbethoxy-derivative of diglycyl-leucine ester (a tripeptide derivative), $EtO\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2Et$.

This method of building up longer chains has, however, its disadvantages, since the condensation becomes more difficult as the higher members are reached, and a new method has consequently been sought for. It was found that the acid chlorides of amino-acids could be prepared by means of thionyl chloride provided that the amino-group is first rendered stable by the introduction of carbethoxyl in the manner stated above. The acid chloride so obtained can then react with the esters of other amino-acids to produce derivatives of the higher members.

Carbethoxyglycylglycine, for example, was in this way converted into the acid chloride, and this reacted with ethyl glycylglycine to give a tetrapeptide derivative, $EtO\cdot CO(NH\cdot CH_2\cdot CO)_3\cdot NH\cdot CH_2\cdot CO_2Et$ (carbethoxytriglycine ester), and in a similar way the mixed dipeptide derivative, carbethoxyglycylalanine, was prepared.

Notwithstanding the wide applicability of this method and the facility with which the changes can be brought about, it could not be said that the final object had been attained, since it is difficult or impossible to obtain the free polypeptides from the carbethoxy-derivatives. Yet another method was therefore devised which has yielded the most excellent results, and is applicable for the synthesis of the most complex polypeptides. It is evident that the limits of this syn-

thetical process have not yet been reached in the compounds described; the operations, in fact, appear to become easier and the yields better as the compounds become more complex.

Briefly stated, this new method consists in acting on the polypeptide or its ester with a halogen-substituted acid chloride, and then, by the action of aqueous ammonia, replacing the halogen in the resulting compound by the amino-group.

The dipeptide, glycylglycine, for example, reacts with chloroacetyl chloride to give chloroacetylglycylglycine, and this, when subjected to the action of aqueous ammonia, even in the cold, gives the tripeptide, diglycylglycine:

$$(NH_2\cdot CH_2\cdot CO)NH\cdot CH_2\cdot CO_2H \longrightarrow ClCH_2\cdot CO\cdot(NH\cdot CH_2\cdot CO)\cdot NH\cdot CH_2\cdot CO_2H \longrightarrow (NH_2\cdot CH_2\cdot CO)(NH\cdot CH_2\cdot CO)NH\cdot CH_2\cdot CO_2H.$$

This tripeptide can now react similarly with chloroacetyl chloride to produce the chloroacetyl derivative, which, in its turn, is changed by ammonia into the tetrapeptide, triglycylglycine,

$$NH_2\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H,$$

and by exactly similar steps this tetrapeptide can be changed to the pentapeptide, tetraglycylglycine,

$$NH_2\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H.$$

The dipeptides hitherto known, glycylglycine, alanylalanine, and leucyl-leucine, were all obtained by the method first described, that is, by fission of the corresponding diketopiperazine; for the preparation, however, of mixed dipeptides, this method is not well adapted, since the piperazine derivatives are in such cases difficult to obtain. By the new process, however, mixed polypeptides can be prepared of apparently any degree of complexity. As examples of some of the mixed forms which have recently been synthesised by Fischer and his colleagues, the following may be mentioned.

i-*Glycylalanine*, $(NH_2\cdot CH_2\cdot CO)\cdot NH\cdot CH(CH_3)\cdot CO_2H$, is obtained, by the steps above mentioned, from chloroacetyl chloride and alanine, and *glycyl*-l-*tyrosin*, $(NH_2\cdot CH_2\cdot CO)\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH$, is prepared similarly from *l*-tyrosine or its ester. The latter dipeptide is easily soluble in water, gives Millon's reaction, and can be hydrolysed by trypsin.

From *l*-tyrosine and α-bromo*iso*hexoyl chloride, *leucyl*-l-*tyrosine* can be obtained, but only in the amorphous state; the corresponding anhydride, $C_4H_9\cdot CH\langle{}^{CO\cdot NH}_{NH\cdot CO}\rangle CH\cdot CH_2\cdot C_6H_4\cdot OH$, however, crystallises in needles.

It has been shown that α-pyrrolidinecarboxylic acid (for which the short name "prolin" is suggested) is a component of most proteid

substances, and it was therefore of especial interest to attempt the synthesis of polypeptides in which the radicle of this acid is contained. A dipeptide of this nature has been prepared by acting on alanine with $\alpha\delta$-dibromovaleryl chloride, $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}COCl$, and decomposing the resulting $\alpha\delta$-dibromovalerylalanine with ammonia. The dipeptide so obtained is called *prolylalanine*, its constitution being

$$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CH(CH_3){\cdot}CO_2H.$$
$$\quad\quad\quad

may not improbably be formed in the successive building up and degradation of albuminous substances.

In the more recent experiments of Fischer and Suzuki, it is shown that cystine readily reacts with halogen-substituted acid chlorides in alkaline solution, and when the products so obtained are treated with ammonia the corresponding polypeptides result. In these reactions, it is found that one molecule of cystine reacts with two molecules of the acid chloride.

Diglycylcystine,

$$(NH_2\cdot CH_2\cdot CO)NH\cdot \underset{\displaystyle CO_2H}{\underset{|}{C}}H\cdot CH_2\cdot S\cdot S\cdot CH_2\cdot \underset{\displaystyle CO_2H}{\underset{|}{C}}H\cdot NH(CO\cdot CH_2\cdot NH_2),$$

is prepared in the above manner from chloroacetyl chloride and cystine. It is a colourless, hard, transparent substance which does not crystallise, is easily soluble in water, and its solution dissolves cupric oxide, giving a blue solution.

Dialanylcystine is similarly obtained from cystine and α-bromopropionyl bromide. The pure product is sparingly soluble, crystallises in microscopic prisms, and is lævorotatory.

Dileucylcystine is obtained in like manner from cystine and α-bromo-*iso*hexoyl chloride. It is fairly easily soluble in cold water and has not been crystallised. The aqueous solution, on evaporation, leaves a glassy residue which, when rubbed, is changed to a colourless powder.

Further, it appeared desirable to attempt the synthesis of polypeptides in which the residues of asparagine or aspartic acid are contained, since, from previous observations, there is little doubt that the latter substances exist in natural proteids in the form of polypeptide-like compounds. Fischer and Koenigs have found that asparagine (and aspartic acids) react with halogen-containing acid chlorides in the usual way, and from the compounds so obtained, by action of ammonia, polypeptides are obtained in which a monobasic acid group replaces hydrogen in the amino-group of asparagine.

Glycylasparagine, $(NH_2\cdot CH_2\cdot CO)\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2$ and *leucylasparagine*,

$$[(CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot CO]\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CONH_2,$$

were in this manner obtained from *l*-asparagine and chloroacetyl and bromo*iso*hexoyl chlorides respectively.

Both of these polypeptides give a strong biuret reaction. In order to obtain polypeptides in which the acid radicle of aspartic acid replaces hydrogen in the amino-group of other amino-acids, chloro- or bromosuccinyl chloride was made to act on an alkaline solution of the amino-acid or its ester. In this case, the resulting halogen-containing product does not act directly in the usual way with ammonia, but gives a fumaryl derivative; the latter, however, by the

action of ammonia at a higher temperature, is transformed into the aspartyl derivative.

Chlorosuccinyldialanine, for example, gives fumaryldialanine, and the latter, when heated to 100° with aqueous ammonia, is changed to the required polypeptide, *aspartyldialanine*,

$[CO_2H{\cdot}CH(CH_3)NH]{\cdot}CO{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO[NH{\cdot}CH(CH_3){\cdot}CO_2H]$.

These fumaryl derivatives can be obtained without first preparing the halogen-substituted succinyl chloride; it is sufficient to act with fumaryl chloride on the ester of the amino-acid, and then saponify the resulting product.

All the results above mentioned tend strongly to confirm the conviction that there is a close resemblance in properties between these artificial polypeptides and the natural peptones; this similarity is especially marked in the case of mixed polypeptides and particularly so in their amides. Amongst some of the reactions in common may be mentioned their precipitation with phosphotungstic acid, the production of the "biuret" reaction with alkaline cupric oxide, and the capability which many of them possess of being hydrolysed by trypsin. Under the influence of the latter ferment, glycyl-*l*-tyrosine yields glycine and *l*-tyrosine, and racemic leucylalanine gives leucyl-*d*-alanine and an active dipeptide which appears to be leucyl-*l*-alanine.

The principal researches of Fischer and his colleagues on the polypeptides will be found in the following papers: *Ber.*, 1901, **34**, 2868; 1902, **35**, 1095; 1903, **36**, 2094, 2106, 2592, 2982; 1904, **37**, 2486, 2842, 3062, 3071, 3103, 3306, 4575, 4585.

The derivatives of several of the above-mentioned polypeptides had been obtained previously by Curtius, although in some cases their true nature has only recently been established. In the year 1881, he showed that by the action of benzoyl chloride on silver glycine three nitrogen-containing acids were formed; one of these proved to be hippuric acid, identical with the natural product, and the others he called the β- and γ-acids. The β-product was later shown to be the benzoyl derivative of glycylglycine, as above mentioned. The γ-acid has recently been further examined by Curtius and Benrath,[1] and is shown to be the benzoyl derivative of pentaglycylglycine,

$$C_6H_5{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CO]_5{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

that is to say, a *hexapeptide* derivative. It may also be prepared by fusing ethyl hippurate with glycine, or its ester may be obtained from the azoimide of benzoyltriglycylaminoacetic acid.

These benzoyl derivatives of polypeptides may be built up link by link by the action of hippurylazoimide on various amino-acids, such as glycine, glycylglycine, aspartic acid, β-aminobutyric acid, &c.

It was stated above that the ethyl ester of glycine undergoes

[1] *Ber.*, 1904, **37**, 1279.

spontaneous decomposition giving glycine anhydride and the "biuret base." This change has now been more minutely examined, and it is found that if moisture is excluded the product consists almost entirely of the biuret base, and that the proportion of glycine anhydride increases as more moisture has access.[1] This biuret base has also been further investigated; Schwarzschild considered it to be the ester of hexaglycylglycine, but Curtius now shows that it is a tetrapeptide derivative, namely, the ethyl ester of triglycylglycine,

$$NH_2 \cdot CH_2 \cdot CO \cdot [NHCH_2CO]_2 \cdot NH \cdot CH_2 \cdot CO_2 \cdot C_2H_5.$$

This base is easily soluble in water and gives many reactions characteristic of proteids. It gives the biuret reaction and produces precipitates with phosphomolybdic acid, tannic acid, lead acetate, &c. Schwarzschild has previously shown[2] that when this base has been subjected to the action of trypsin for 4—6 days it no longer gives any biuret reaction.

Analytical Processes.

The two following processes are described in the report on analytical chemistry.

(i) The rapid ultimate analysis of certain carbon compounds[3] (p. 156).

(ii) The determination of methyl alcohol in presence of ethyl alcohol[4] (p. 166).

A new and simple method for the determination of acetyl groups is given by A. G. Perkin.[5] The substance to be examined is distilled with alcohol and sulphuric acid, and the resulting ethyl acetate is collected in standard alcoholic potash and determined by titration.

For the determination of hydroxyl groups in organic compounds, Tschugaeff, in 1902, proposed a method based on the estimation of the amount of methane evolved when the compound is acted on in ethereal solution by magnesium methyl iodide, according to the relation

$$ROH + CH_3 \cdot MgI = RO \cdot MgI + CH_4.$$

Hibbert and Sudborough have carefully examined this method and find that, in order to obtain reliable results, it is advisable to use amyl ether as solvent in place of ethyl ether, and to carry out the operations in an atmosphere of nitrogen.[6]

Pringsheim[7] and von Konek[8] recommend the use of sodium peroxide

[1] Curtius, *Ber.*, 1904, **37**, 1284.
[2] *Beitr. chem. Physiol. Path.*, 1903, **4**, 155.
[3] Collie, *Trans.*, 1904, **85**, 1111.
[4] Thorpe and Holmes, *ibid.*, 1.
[5] *Proc.*, 1904, **20**, 171.
[6] *Trans.*, 1904, **85** 933.
[7] *Ber.*, 1904, **37**, 2155.
[8] *Zeit. angew. Chem.*, 1904, **17**, 886.

for the detection and estimation of halogens, phosphorus, arsenic, and sulphur in organic compounds. For this purpose, it is recommended that the peroxide should be mixed with about 25 times its weight of some substance rich in carbon and hydrogen which is not hygroscopic, such as naphthalene or cinnamic acid; this mixture can then be stored ready for use in a closed flask. Even carbon may be estimated, according to von Konek, by determining the amount of carbonate formed when the organic substance is oxidised with sodium peroxide.

For the dehydration and preservation of ethyl alcohol, Evans and Fetsch[1] suggest the use of magnesium amalgam, which is easily obtained by rubbing together mercury and powdered magnesium, the latter being added gradually. This amalgam is without action on cold absolute ethyl alcohol, but reacts instantly with water. When heated with methyl or ethyl alcohols, the corresponding magnesium methoxide or ethoxide are produced, the former being soluble and separating in the crystalline form on cooling.

The conditions under which the "pyrrole reaction" is given by various substances, may, according to Neuberg,[2] afford useful information for their identification.

He divides the substances under consideration into four classes: (1) those which give the reaction directly (pyrrole, indole, carbazole); (2) nitrogen-containing substances which, when decomposed by heating, give off vapours capable of showing the reaction (certain amino-acids and ammonium salts, such as glutamic acid, cystine, serine, taurine, ammonium malate and pyruvate, &c.); (3) nitrogen-containing substances which yield the reaction only when heated with zinc dust (glucosamine, glucose-oxime, erythrose diacetamide, and ammonium salts of gluconic, tartaric, oxalic, and malonic acids); (4) nitrogen-free oxygen-containing substances which give pyrrole when heated with ammonia or ammonium salts (γ-diketones).

H. J. H. Fenton.

[1] *J. Amer. Chem. Soc.*, 1904, **26**, 1158.
[2] *Chem. Centr.*, 1904, ii, 1435.

ORGANIC CHEMISTRY—AROMATIC AND OTHER CYCLIC DIVISIONS.

In reviewing the year's work in so wide, varied, and fertile a field of research as that of the chemistry of the aromatic compounds, it is a difficult task to indicate which region has yielded the most abundant or the most luxuriant harvest. The ground most assiduously cultivated is naturally that which is related to the industries based on organic chemistry.

Although the development in the field of colour chemistry has followed the old lines, there has been no diminution in the crop of new dye-stuffs. On the theoretical side, the study of the relation of colour to structure, always a fascinating subject for speculation, has received more than its usual share of attention, and appears rather to grow than to diminish in complexity. Whilst a strong case has been made out for the existence of a quinonoid ion in members of the triphenylmethane and allied dyes, the total absence of colour in the quinoneimines and the existence of true dye-stuffs with an open chain structure is opposed to any general application of a quinone structure to every class of colouring matters.

In the region of synthetical chemistry, a powerful stimulus has been offered by the elaboration of new reactions as well as by the modification of old ones. In the latter case, the tendency lies in the direction of milder reagents. Given a compound in a labile state, a catalyst of the most insipid kind may prove a powerful instrument of chemical change. The lability of vital products is the *primum movens* of their rapid and complex evolutions under conditions which might seem to exclude chemical agency altogether.

The conductivity of mineral acids in ethereal solution touches the fringe of important applications of physical chemistry to organic reactions, which promise an interesting development.

The unique character of Gomberg's tervalent carbon compound, taken in conjunction with the significance of its double molecular formula, demand for the present an open verdict on its structure until further evidence is forthcoming.

The subjects of the report have been grouped in sections so as to permit of general treatment and scarcely require explanation.

New Reagents.

The use of dimethyl sulphate as a methylating agent, which was introduced by Ullmann,[1] and has proved so serviceable in preparing methyl derivatives of hydroxy- and amino-compounds and of sulphonic acids, can also be used in the preparation of methyl esters from acids where the usual methods fail.[2]

The well-known Schotten-Baumann method of acylating, in which the acid chloride is used in presence of alkali, can be modified with advantage in many cases by replacing the alkali by pyridine. The modified reaction has been widely applied.[3] Recent papers on the subject by Freundler[4] deal with the acylation of alcohols and amino-compounds, whilst Auwers[5] has shown that hydroxy-compounds with basic substituents like the hydroxybenzylarylamines (I) and aromatic hydroxyaldehydephenylhydrazones (II) produce, in presence of pyridine, *O*-esters, when under ordinary circumstances *N*-esters would be formed :

I.

II.

Heller[6] finds, moreover, that acylated compounds containing the group N·CN, which are usually unstable when alkalis are used, can be readily obtained with pyridine.

The substitution of ammonia for the caustic alkalis and alkyl oxides, which bears a certain analogy to the above, is dealt with under "condensation" on p. 98.

The action of potassium cyanide on aromatic nitro-compounds produces a very complex series of changes which have been exhaustively studied by Lobry de Bruyn.[7] The action may be of a three-fold character. The cyanide may act as a reducing agent and form azo-, azoxy-, nitroso-, and amino-compounds, or, if the reaction proceeds in alcoholic solution, the replacement of a nitro-group by an alkyloxy-group may occur, or, thirdly, one or more cyanogen groups may enter the nucleus whereby either a nitro-group or hydrogen is replaced. In an interesting series of memoirs on a similar subject, namely, the action of potassium cyanide on nitrophenols, the constitution of the purpuric acids is discussed by Borsche

[1] *Annalen*, 1903, **327**, 104.
[2] Werner and Seybold, *Ber.*, 1904, **37**, 3658; H. von Liebig, *Ber.*, 1904, **37**, 4036.
[3] Einhorn and Hollandt, *Annalen*, 1898, **301**, 96.
[4] *Bull. Soc. chim.*, 1904, [iii], **31**, 616, 621.
[5] *Ber.*, 1904, **37**, 3899. [6] *Ibid.*, 3112. [7] *Rec. Trav. chim.*, 1904, **23** 26.

and Locatelli and Borsche and Böcker.[1] The papers are too long to review, but it may be stated that here also cyanogen appears to enter the nucleus and that a nitro-group undergoes reduction to a hydroxylamine group.

A curious reaction of potassium cyanide has been observed by Wolff and Lindenhayn[2] in connection with diazoacetophenone and diazobenzeneimide. With the former a salt of acetophenoneazocyanide, and with the latter phenylcyanotriazine, is formed :

$$C_6H_5\cdot CO\cdot CH\!<\!\overset{N}{\underset{N}{\|}} + HCN = C_6H_5\cdot CO\cdot CH_2\cdot N{:}N\cdot CN.$$

Acetophenoneazocyanide.

$$C_6H_5\cdot N\!<\!\overset{N}{\underset{N}{\|}} + HCN = C_6H_5\cdot N{:}N\cdot NH\cdot CN.$$

Phenylcyanotriazine.

The use of potassium cyanide in the formation of additive compounds, to which this reaction strictly belongs, is referred to again on p. 102.

Von Braun[3] uses cyanogen bromide for preparing cyanobenzenesulphonamides by adding the reagent to the sodium compound of the sulphonamide. Benzenesulphonanilide gives $C_6H_5\cdot SO_2(N\cdot C_6H_5)\cdot CN$. The same reagent is used for obtaining a new class of dyes, which promise to be of some importance (p. 128).

The action of nitriles on carboxylic acids, which was first studied by Gautier, has been very fully investigated by König.[4] The reaction takes place in the following way :

$$R\cdot C{:}N + HO\cdot CO\cdot R' \rightarrow R\cdot \underset{OH}{C}{:}N\cdot CO\cdot R' \rightarrow R\cdot CO\cdot NH\cdot CO\cdot R'.$$

Anthranilic acid also combines with nitriles, but forms at the same time a quinazoline derivative by inner condensation. Very important from a technical, as well as a theoretical, standpoint is the action of the alkali sulphites on aromatic amino- and hydroxy-compounds, which forms the subject of a series of papers by Bucherer.[5] The reaction may be divided into the following three categories.

1. By the action of bisulphite solutions on aromatic amino-compounds the latter lose ammonia and are converted into new substances, which, on hydrolysis, break up into the corresponding aromatic hydroxyl compounds and sulphurous acid, which is eliminated. The intermediate

[1] *Ber.*, 1902, **35**, 569 ; 1904, **37**, 1843, 4388.
[2] *Ibid.*, 1904, **37**, 2374. [3] *Ibid.*, 2809.
[4] *J. pr. Chem.*, 1904, [ii], **69**, 1.
[5] *Ibid.*, 49 ; **70**, 345 ; *Zeit. Farb. Text. Ind.*, 1904, **3**, 57.

compound may consequently be regarded as the sulphurous ester of the hydroxyl compound :

$$R{\cdot}NH_2 + 2NaSO_3H = R{\cdot}O{\cdot}SO_2H + Na_2SO_3 + NH_3.$$

2. Bisulphite solutions convert aromatic hydroxyl compounds into the above sulphurous esters :

$$R{\cdot}OH + 2NaSO_3H = R{\cdot}O{\cdot}SO_2H + Na_2SO_3 + H_2O.$$

3. Ammonium sulphite solution in presence of ammonia converts aromatic hydroxyl compounds into the corresponding amino-compounds, a process which is probably determined by the formation of the intermediate sulphurous ester above referred to. The reaction can be expressed by the following equation :

$$R{\cdot}OH + (NH_4)_2SO_3 + NH_3 = R{\cdot}NH_2 + (NH_4)_2SO_3 + H_2O.$$

It should be added that the sulphites of aliphatic amino- and hydroxy-compounds do not react as above described, and, moreover, the benzene derivatives show less reactivity than those of naphthalene. The reaction appears to depend on the stability of the sulphurous ester, which is affected not only by the character, but also by the substituents of the nucleus. The position of the sulphonyl group in the sulphonic acids, for example, has a marked influence, sometimes retarding, at others assisting the reaction. A number of experimental details are given showing the conversion of naphthylamine and its sulphonic acids into the corresponding naphthol compounds and the reverse change from naphthols into naphthylamine derivatives.

It appears, moreover, that by acting on β-naphthol and β-naphthylamine and their derivatives with aromatic amino-compounds in presence of bisulphite they pass into secondary or aryl-substituted β-naphthylamines, forming, as before, sulphurous esters as intermediate products in the following way :

$$\text{I, } R^{\beta}{\cdot}OH + HO{\cdot}SO_2Na = R{\cdot}O{\cdot}SO_2Na + H_2O$$
$$\text{or } R^{\beta}{\cdot}NH_2 + HO{\cdot}SO_2Na = R{\cdot}O{\cdot}SO_2Na + NH_3 ;$$
$$\text{II, } H_2NR' + R{\cdot}O{\cdot}SO_2Na = R{\cdot}NHR' + NaHSO_3.$$

Metals and metallic compounds are coming more and more into use as organic reagents, acting, as a rule, the part of catalysts. The use of metals as "halogen carriers" and of copper in Sandmeyer's reaction are too well known to need description. Ullmann and his collaborators [1] have recently shown that finely-divided copper may be used for removing halogens from the nucleus of aromatic compounds. The halogen, which is usually regarded as so firmly attached as to defy the attack of most reagents, may by this means be simply removed or sub-

[1] *Ber.*, 1903, **36**, 2383 ; 1904, **37**, 853 ; *Annalen*, 1904, **332**, 38.

stituted by amino- and phenoxyl groups. Good yields of diphenyl (and its derivatives) have been obtained from iodobenzene (and its derivatives) by heating the substances with copper in a fine state of division to 210—220°, either in closed or, if the boiling point is high enough, in open vessels. A technical application of this discovery is the subject of a patent for the preparation of anthranilic acid and derivatives from *o*-chlorobenzoic acid and the amines in presence of copper. The use of finely-divided nickel as a reducing agent is described on p. 93.

Dewar and Jones[1] have found that nickel carbonyl acts on benzene in presence of aluminium chloride and converts it, at the ordinary temperature, mainly into benzaldehyde. At 100° the principal product is anthracene. Other aromatic hydrocarbons behave similarly.

Eijkman[2] has utilised Friedel and Crafts' method for the synthesis of aromatic acids from lactones. For example, γ-methylbutyrolactone with benzene and aluminium chloride yields phenyl-γ-methylbutyric acid, $C_6H_5 \cdot C(CH_3) \cdot CH_2 \cdot CH_2 \cdot CO_2H$. Another interesting application of the same reaction is the preparation of benzeneazodiphenyl, $C_6H_5 \cdot N_2\ C_6H_4 \cdot C_6H_5$, and its homologues by the action of aluminium chloride on a mixture of azoxybenzene (or its homologues) and the aromatic hydrocarbon.[3]

Grignard's Reaction.—The importance of Grignard's reaction as an invaluable aid to organic synthesis has become more emphasised with further study, and no less than fifty separate investigations in connection with the aromatic compounds alone have appeared during the present year. Of these, Grignard[4] has contributed one on the preparation of tertiary alcohols from esters. The compound R·CO·OMgX is first prepared in the usual way, and a second molecule, R′MgX, is then added in the cold. The mixture is heated on the water-bath and ultimately decomposed with dilute sulphuric acid, when the tertiary alcohol CRR′·OH is formed according to the following equation:

$$R \cdot CO \cdot OMgX + R'MgX = CRR'(OMgX)_2.$$
$$CRR'(OMgX)_2 + R'MgX = CRR_2'OMgX + (MgX)_2O.$$

Phenyldiethylcarbinol and diphenylethylcarbinol have been obtained in this way.

A number of papers[5] which describe the formation of aromatic secondary and tertiary alcohols from aldehydes and ketones afford little novelty except in the application of the method, but the new carbinol derivatives containing a naphthalene, anthracene, or acridine

[1] *Trans.*, 1904, **85**, 212.
[2] *Chem. Weekblad*, 1904, **1**, 421.
[3] Anz, *Bull. Acad. Sci. Cracow*, 1904, 158.
[4] *Compt. rend.*, 1904, **138**, 152.
[5] Acree, *Ber.*, 1904, **37**, 990; Bistrzycki and Gyr, *Ber.*, 1904, **37**, 1245; Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 228; Mameli, *Gazzetta*, 1904, **34**, [i], 358.

nucleus are sufficiently rare to merit a short description. Magnesium α-naphthyl bromide, $C_{10}H_7MgBr$, and benzophenone yield diphenyl-α-naphthylcarbinol, $C_{10}H_7 \cdot C(C_6H_5)_2 \cdot OH$; this, like the other triarylcarbinols, is colourless, but becomes deeply coloured (greenish-blue) by adding strong sulphuric acid or acetic and hydrochloric acids (see p. 129). On reduction with tin and hydrochloric acid, it is converted like triphenylcarbinol into the corresponding methane derivative.[1] Anthraquinone and magnesium phenyl bromide form γ-dihydroxy-γ-diphenylhydroanthracenes:[2]

$$C_6H_4\begin{<}{CPh(OH)}{CPh(OH)}\end{>}C_6H_4.$$

Diphenylanthrone (I) and magnesium phenyl bromide give in the same way γ-triphenyl-γ-hydroxydihydroanthracene (II):[3]

$$C_6H_4\begin{<}{CO}{CPh_2}\end{>}C_6H_4 \qquad C_6H_4\begin{<}{CPh(OH)}{CPh_2}\end{>}C_6H_4.$$

I. II.

The formation of a hydroxydihydro-base from *N*-methylacridone belongs to the same class of reactions. Magnesium phenyl bromide converts *N*-methylacridone (III) into hydroxyphenyl-*N*-methyldihydroacridine (IV):[4]

$$C_6H_4\begin{<}{CO}{NMe}\end{>}C_6H_4 \qquad C_6H_4\begin{<}{CPh(OH)}{NMe}\end{>}C_6H_4.$$

III. IV.

Dialkylphthalides are readily obtained by the action of magnesium alkyl compounds on phthalic anhydride. Dimethyl- and diethylphthalides have been prepared in this way:[5]

$$C_6H_4\begin{<}{C(CH_3)_2}{CO}\end{>}O.$$

Dimethylphthalide.

Lactones behave similarly.[6] Phthalimide, however, gives a somewhat different result and yields derivatives of phthalimidine[7] as follows:

$$C_6H_4\begin{<}{CO}{CO}\end{>}NH + 2C_2H_5 \cdot MgBr =$$

$$CO\begin{<}{C_6H_4}{NMgBr}\end{>}C(C_2H_5) \cdot OMgBr + C_2H_6.$$

$$CO\begin{<}{C_6H_4}{NMgBr}\end{>}C(C_2H_5) \cdot OMgBr + H_2O =$$

$$CO\begin{<}{C_6H_4}{NH}\end{>}C{:}CH \cdot CH_3 + MgBr_2 + Mg(OH)_2.$$

[1] Acree, *Ber.*, 1904, **37**, 616, 625, 2753.
[2] Haller and Guyot, *Compt. rend.*, 1904, **138**, 327.
[3] Haller and Guyot, *ibid.*, **139**, 9.
[4] Bünzly and Decker, *Ber.*, 1904, **37**, 575.
[5] Bauer, *ibid.*, 735. [6] Houben, *ibid.*, 489.
[7] Béis, *Compt. rend.*, 1904, **138**, 987; **139**, 61.

Magnesium phenyl bromide gives the phenylcarbinol compound :

$$CO<\begin{matrix}C_6H_5\\NH-\end{matrix}>CPh\cdot OH.$$

The alkylsaccharins, which belong to the same group of substances as the phthalimides, yield similar products.[1] Unsaturated compounds, as secondary products caused by the removal of water from the original carbinol, have been obtained by Hell and Bauer, Klages, and others [2] by the help of this reaction.

Anisylphenylketone and magnesium ethyl iodide give anisylphenylpropylene, $CH_3\cdot O\cdot C_6H_4\cdot C(C_6H_5){:}CH\cdot CH_3$. So also anisaldehyde and magnesium benzyl bromide give directly *p*-methoxystilbene without the formation of carbinol, whereas acetophenone and magnesium benzyl bromide form phenylbenzylmethylcarbinol,

$$C_6H_5\cdot CH_3\cdot C(OH)\cdot CH_2\cdot C_6H_5,$$

which, only after heating with acetic anhydride, passes into α-methylstilbene.

As these unsaturated hydrocarbons can be reduced with sodium and alcohol, the reaction affords a simple method for preparing aryl paraffins.[3] Schroeter and also Tiffeneau have utilised Grignard's reaction for preparing unsaturated acids. Acetophenone and ethyl iodoacetate in presence of magnesium give the ester of hydroxy-acid which, on distillation under the ordinary pressure, is converted into β-methylcinnamic acid.[4] Unsaturated phenols with a pseudoallyl side-chain,

$$R\cdot C(CH_3){:}CH_2,$$

have been obtained from the corresponding esters by using excess of magnesium methyl iodide in the following way : [5]

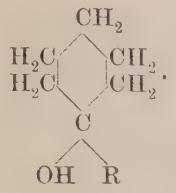
$$CR(CH_3)_2\cdot OMgI + Mg(CH_3)I = CR(CH_3){:}CH_2 + MgI_2 + MgO + CH_4.$$

The action of ethyl orthoformate on the organomagnesium compound has been employed in the synthesis of acetals and indirectly of aldehydes of the aromatic series,[6]

$$HC(OR)_3 + R'MgI = R'CH(OR)_2 + RO\cdot MgI.$$

Sabatier and Mailhe [7] have prepared from *cyclo*hexanone a series of tertiary alcohols having the general formula :

[1] Sachs, Wolff, and Ludwig, *Ber.*, 1904, **37**, 3252.
[2] Hell and Stockmayer, *ibid.*, 225 ; Hell and Bauer, *ibid.*, 230, 453, 1429.
[3] Klages and Heilmann, *ibid.*, 1447.
[4] Tiffeneau, *Compt. rend.*, 1904, **138**, 985 : Schroeter, *Ber.*, 1904, **37**, 1090.
[5] Béhal and Tiffeneau, *Compt. rend.*, 1904, **139**, 139.
[6] Bodroux, *ibid.*, **138**, 92, 700 ; Tschitschibabin, *Ber.*, 1904, **37**, 186, 850.
[7] *Compt. rend.*, 1904, **138**, 139, 343, 1321.



The introduction of alkyl groups into hydrocyclic compounds by Grignard's method has also been successfully employed by Perkin in the synthesis of terpin, terpineol, and dipentene, to which reference is made on p. 117.

The formation of glycols and pinacones has also been effected by this reaction.

Acree has prepared benzpinacone, $(C_6H_5)_2C(OH)\cdot C(OH)(C_6H_5)_2$, from phenylbenzoin and magnesium phenyl bromide, as well as from benzil or methyl benzilate and magnesium phenyl bromide. Benzoin or methyl mandelate produce in the same way $\alpha\alpha\beta$-triphenylethylene glycol,

$$(C_6H_5)_2C(OH)\cdot CH(OH)\cdot C_6H_5.$$[1]

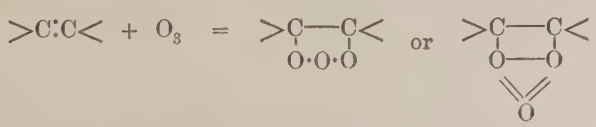
Dilthey and Last [2] have also obtained benzpinacone from magnesium phenyl bromide and ethyl oxalate.

An interesting synthesis of an optically active alcohol has been effected by Frankland and Twiss by the action of magnesium phenyl bromide on dimethyl tartrate.[3] The $\alpha\alpha\delta\delta$-tetraphenylerythritol which is formed has a specific rotation of $[\alpha]_D^{20^\circ} + 182{\cdot}8^\circ$.

Finally, Kipping,[4] Dilthey and Eduardoff,[5] Pfeiffer and Schnurmann and Truskeier [6] have shown that Grignard's reaction may be employed in the preparation of aryl and alkyl compounds of silicon and the metals.

Oxidising Agents.

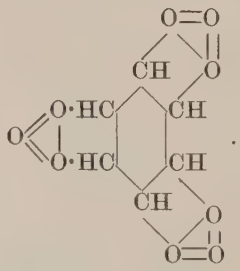
In former papers, Harries has shown that by means of ozone alcohols may be oxidised to aldehydes, iodobenzene to iodosobenzene, and unsaturated compounds may be ruptured at the double bond and converted into aldehydes and ketones. If, however, the ozone is allowed to react in a non-dissociating solvent, oxygen is added at the double bond with the formation of compounds having the following formulæ:



These ozonides are decomposed with water into two molecules of

[1] *Ber.*, 1904, **37**, 2753.
[2] *Ibid.*, 3775.
[3] *Trans.*, 1904, **85**, 1666.
[4] *Proc.*, 1904, **20**, 15.
[5] *Ber.*, 1904, **37**, 1139.
[6] *Ibid.*, 319, 1125.

ketone and hydrogen peroxide. The same result is produced by the action of ozone on the unsaturated compound in presence of water. The ozonides are viscid, colourless, or light green oils, with a suffocating smell. The ozonides of mesityl oxide and acrolein are highly explosive, whilst those of the unsaturated hydrocarbons are, on the other hand, more stable and only explode on heating on platinum foil. The ozonides possess the curious property of emitting rays which act more strongly on the photographic plate than ozone itself.[1] Harries and his collaborators [2] have used ozone for determining the position of the double bond in unsaturated hydrocarbons, and have employed it with advantage in breaking down the caoutchouc molecule into simpler constituents.[3] More recently, Harries and Weiss [4] have succeeded in analysing Renard's ozobenzene, which the latter obtained by the action of ozone on benzene. The compound is benzenetriozonide, to which Harries assigns the following formula :



It is obtained by passing a current of oxygen containing 5 per cent. of ozone for 1—2 hours into pure benzene. A gelatinous, opalescent product is formed, which, on removing the benzene, remains as a white, amorphous substance. It explodes violently when warm water is poured upon it ; but when carefully warmed with water, it passes slowly into solution as glyoxal.

The oxidising action of fuming sulphuric acid in presence of mercury, which is used in the production of phthalic acid from naphthalene, is the subject of two patents, one for oxidising anthracene to anthraquinone and the other for converting anthraquinone-β-sulphonic acid into a new polyhydroxyanthraquinonesulphonic acid.

Electrolytic methods both for oxidation and reduction are rapidly gaining in importance. The oxidation of anthracene and naphthalene to the quinones has been effected by electrolysis in an acid solution containing cerium salts, and A. G. and F. M. Perkin [5] describe an electrolytic method for producing purpurogallin from pyrogallol and its carboxylic acid from gallic acid.

[1] *Ber.*, 1904, **37**, 839.
[2] *Ibid.*, 842.
[3] *Ibid.*, 2708.
[4] *Ibid.*, 3431.
[5] *Trans.*, 1904, **85**, 243.

Reduction.—Two patents connected with electrolytic reduction have been applied for in the course of the year, one for converting nitrobenzene into *p*-aminophenol in the manner described by Gattermann, and the other for the production of aromatic and aliphatic amino-bases by the electrolysis of an aldehyde in presence of ammonia or an amine. For example, formaldehydeaniline yields on electrolysis methylaniline; acetaldehyde and ethylamine are converted into diethylamine. Electrolytic methods for the reduction of aliphatic and aromatic acids and esters are described by Tafel and Friedrichs [1] and C. Mettler.[2] The reducing action of nickel in presence of hydrogen, introduced recently by Sabatier and Senderens [3] and used by them for the reduction of a variety of aliphatic compounds, has during the past year been successfully applied to the preparation of *cyclo*hexanols from phenols and *cyclo*hexylamines from aromatic bases. By passing phenol vapour mixed with excess of hydrogen over nickel at 215—230°, the phenol is reduced to *cyclo*hexanol, which is at the same time partly converted into *cyclo*hexanone by the loss of hydrogen. The mixed product may be either wholly converted into alcohol by passing it a second time over nickel with excess of hydrogen at a lower temperature (140—150°), or into the ketone by conducting the vapour without hydrogen over copper heated to 330°. Other *cyclo*hexanols have been prepared by Brunel [4] by this method. The new hydrocyclic alcohols are colourless liquids with characteristic odours: *cyclo*hexanol boils at 160—161°.[5]

In the same way, when aniline vapour and hydrogen are passed over finely-divided nickel heated to 190°, a mixture of nearly equal parts of *cyclo*hexylamine, $C_6H_{11}\cdot NH_2$, di*cyclo*hexylamine, $C_6H_{11}\cdot NH\cdot C_6H_{11}$, and *cyclo*hexylaniline, $C_6H_5\cdot NH\cdot C_6H_{11}$, are formed; *cyclo*hexylamine is a colourless liquid with an ammoniacal smell resembling conicine; it is a strong base which absorbs carbon dioxide from the air and forms crystalline salts. The alkylanilines and *m*-toluidine have been reduced in the same way.

Godcot [6] has converted anthracene by Sabatier and Senderens' method into tetrahydro- and octohydro-anthracenes.

Acree [7] has found a new method for reducing triphenylcarbinol and triphenylchloromethane and their homologues to the methane hydrocarbons without the formation of hexaphenylethane. Triphenylmethyl (see p. 105), which is probably first liberated, very readily polymerises in presence of hydrochloric acid to hexaphenylethane; but by using spongy tin and gradually adding the calculated amount of hydrochloric acid, polymerisation is avoided and the reduction proceeds smoothly.

[1] *Ber.*, 1904, **37**, 3187.
[2] *Ibid.*, 3692.
[3] *Compt. rend.*, 1904, **137**, 1025; **138**, 457, 1257.
[4] *Ibid.*, **137**, 1268.
[5] Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, 201.
[6] *Compt. rend.*, 1904, **139**, 604.
[7] *Ber.*, 1904 **37**, 811.

Chlorination.—Von Braun[1] has succeeded in obtaining amidochlorides from aromatic amides by the action of phosphorus pentachloride in chloroform or other suitable solvent, from which the new substance may be precipitated with light petroleum:

$$R_1CO\cdot NR_2 + PCl_5 = R_1C(Cl_2)NR_2 + POCl_3.$$

Amidines can be obtained from them by the action of arylamino-compounds in the ordinary way. Dimethylbenzamide, for example, gives the dichloride, $C_6H_5\cdot CCl_2\cdot N(CH_3)_2$, which, with aniline, is transformed into the amidine, $C_6H_5\cdot C(N\cdot C_6H_4)\cdot N(CH_3)_2$. Now the dichlorides are unstable at high temperatures and lose alkyl chloride, as von Pechmann first pointed out, so that if dimethylbenzamide is heated with phosphorus pentachloride, methyl chloride escapes and methylbenzimido-chloride, $C_6H_5\cdot CCl{:}N\cdot CH_3$, is produced. At a still higher temperature, a second molecule of methyl chloride is driven off, and benzonitrile finally remains. The application of this reaction to acyl derivatives of cyclic amines has led to interesting results; for, under certain conditions, the ring opens and aliphatic products are formed. Benzoylpiperidine (I) with phosphorus pentachloride is either decomposed into benzimido-chloride of ε-chloroamylamine (II), which readily changes into benzoyl-ε-chloroamylamine (III), or it produces a mixture of benzonitrile and 1:5-dichloropentane (IV). 1:5-Dibromopentane can be obtained in a similar manner:

$$C_6H_5\cdot CO\cdot N\begin{<}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{>}CH_2 \longrightarrow \underset{\text{II.}}{C_6H_5\cdot CCl{:}N(CH_2)_5Cl}$$

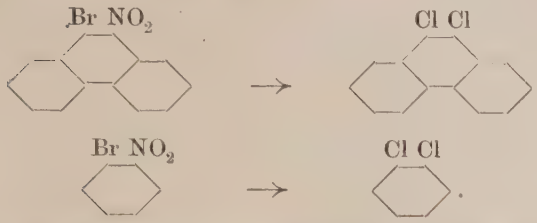
(I.)

$$\longrightarrow \underset{\text{III.}}{C_6H_5\cdot CO\cdot NH(CH_2)_5Cl} \quad \text{or} \quad \underset{\text{IV.}}{(CH_2)_5Cl_2}$$

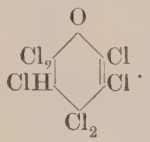
In a later paper, von Braun shows how piperidine may be converted into pentamethylenediamine and pimelic acid by means of this reaction. Alkali hypochlorites as chlorinating agents have been applied by Chattaway to the preparation of nitrogen chlorides of the general formula $R\cdot SO_2\cdot NCl_2$, and chloroamides of the formula $R_1\cdot SO_2\cdot NCl\cdot R_2$.[2]

A curious process of chlorination by substitution is described by Schmidt and Ladner.[3] When 9:10-bromonitrophenanthrene or *o*-bromonitrobenzene is heated in sealed tubes to 320° with ammonium chloride, both bromine atom and nitro-group are replaced by chlorine, and satisfactory yields of the dichloro-compounds are obtained:

[1] *Ber.*, 1904, **37**, 2678, 2812, 2915, 3210, 3583, 3588.
[2] *Trans.*, 1904, **85**, 971.
[3] *Ber.*, 1904, **37**, 4402.

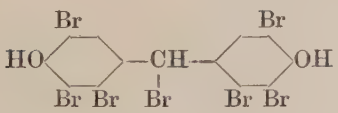


The product formed by the chlorination of salicylaldehyde is heptachloroketotetrahydrobenzene :

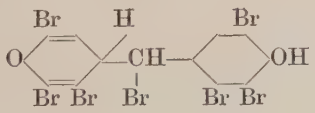


Biltz and Giese[1] find that on reduction with stannous chloride and hydrochloric acid a quantitative yield of tetrachlorophenol is obtained. By boiling the same product with dilute acetone, 90 per cent. of pure pentachlorophenol is produced.

Bromination.—The action of bromine on *p*-hydroxy- and dihydroxy-diphenylmethanes forms the subject of several long communications by Zincke and his collaborators[2] in continuation of their previous researches on the bromination of phenols. Only a brief summary of these papers can be given Di-*p*-hydroxydiphenylmethane combines in acetic acid solution with four atoms of bromine. When treated in the cold with bromine, it takes up two additional atoms. The hexabromide is colourless and unchanged by alkalis. If it is heated with bromine in a sealed tube, a seventh bromine atom can be introduced, and enters the methylene group (I or II) :



I.

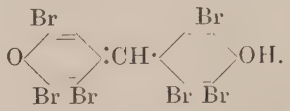


II.

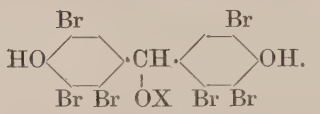
This substance no longer possesses the properties of a normal bromide, but, according to Zincke, those of a pseudo-bromide ; for it reacts with alcohols, acetone, and aniline, forming compounds which dissolve in alkalis. The product formed by the action of a small quantity of methyl alcohol on the heptabromide, or by adding water

[1] *Ber.*, 1904, **37**, 4010.
[2] *Annalen*, 1904, **330**, 61 ; **334**, 342, 367.

to the acetone solution, is hexabromohydroxybenzylidenequinone, and possesses the following structure :

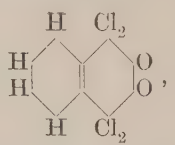


It crystallises in red needles. Its quinonoid character is determined by the additive compounds which it forms, and which are the same as those obtained by the direct action of the same reagents on the heptabromide. These compounds have the general formula,

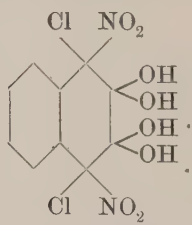


in which OX = OH, O·CH_3, O·C_6H_5, NH·C_6H_5. They dissolve in alkali without change, forming colourless solutions. The heptabromide is completely reduced to the hexabromide with hydriodic acid. When zinc and hydrochloric acid, on the other hand, act on an ethereal solution of the heptabromide, the reduction proceeds slowly, and the product contains a substance which gives a violet colour with alkali. The author regards this compound as the quinonoid form of the hexabromide.

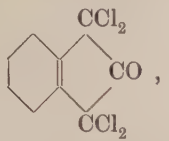
In a later paper, Zincke and Fries have studied the action of chlorine and bromine on 2 : 3-dihydroxynaphthalene. When excess of chlorine is present, the tetrachlorodiketo-derivative is first formed,



which on reduction yields a dichlorodihydroxynaphthalene. The latter, when acted on by strong nitric acid in the cold, forms a curious compound, to which the following formula is provisionally assigned :

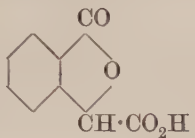


Bleaching powder converts the tetrachlorodiketone into the corresponding hydrindene derivative, which, with alkalis,

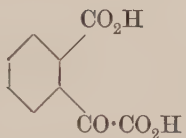


Tetrachloroketohydrindene.

breaks up into phthalidecarboxylic acid, and on oxidation with nitric acid into phthalonic acid,



Phthalidecarboxylic acid.

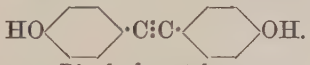


Phthalonic acid.

The action of bromine on 2 : 3-dihydroxynaphthalene gives similar results to the above.

In a former paper[1] these authors investigated the action of chlorine and bromine on stilbene. In a later communication,[2] the action of these reagents on di-*p*-acetoxystilbene has been studied. An additive compound is first formed, having the following general formula, in which X = Cl or Br, and exists in two isomeric forms, like the stilbene derivative :

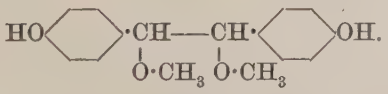
The less fusible modification, on heating, loses halogen hydride, and is converted into di-*p*-acetoxystilbenemonohalide, which, with alcoholic potash, loses a further molecule of halogen hydride whilst undergoing simultaneous hydrolysis, and yields di-*p*-hydroxytolane :



Di-*p*-hydroxytolane.

Dihydroxytolane dissolves in strong sulphuric acid to a red solution, which is probably due to the formation of a quinonoid compound.

When methyl-alcoholic potash acts on either modification of the halogen additive compound of diacetoxystilbene, the same methoxy-derivative is produced :



The dibromide additive compound of di-*p*-hydroxystilbene, which has the properties of a pseudo-bromide, is decomposed by water into stilbene-

[1] *Annalen*, 1902, **325**, 19, 44. [2] *Ibid.*, 1904, **335**, 157.

quinone, a highly reactive substance which crystallises in bright red needles:

The two forms probably correspond to hydro- and *iso*hydro-benzoin, and the same compound is produced when strong sulphuric acid acts on the halogen additive compound of diacetoxystilbene with the elimination of acetyl halide.

The bromination of phenols has been studied by Hewitt, Kenner, and Silk,[1] who find that when one molecular proportion of bromine acts on ordinary phenol the character as well as the relative quantities of the products vary with the conditions. Absence of water and presence of strong mineral acids favour the formation of *p*-bromophenol. If more than one molecular proportion of bromine is added to phenol dissolved in strong sulphuric and glacial acetic acids, the second molecule of bromine is utilised very slowly, the sulphuric acid hindering substitution in the ortho-position; but with excess of 73 per cent. sulphuric acid the action takes place readily, and 2 : 4-dibromophenol is obtained.

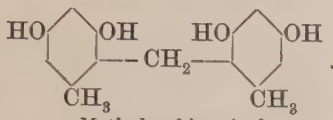
Condensation.

Among the various reagents which have been employed to effect condensation, perhaps the most interesting, because of the possible insight they afford into the synthetical agents used by the living organism, are ammonia and the primary and secondary amines (diethylamine and piperidine). A summary of the various condensation products obtained by this means between aldehydes on the one hand and 1 : 3-diketones and similar compounds on the other is given by Knoevenagel,[2] who has himself made a comprehensive study of this reaction. The range of compounds with which aldehydes condense includes substances having the formula $RCH_2 \cdot NO_2$, like nitroethane and phenylnitroethane, and also 2 : 4-dinitrotoluene. Ketones condense with ethyl cyanoacetate, ethyl acetoacetate, and again ethyl cyanoacetate condenses with unsaturated ketones, like dibenzylideneacetone, ethyl fumarate, and carvone, forming products having the nature of additive compounds.

Products of the condensation of formaldehyde with aromatic compounds have been the subject of numerous memoirs and patents. In the past year, the following papers, among others, have appeared on the subject. Condensation products of phenols with formaldehyde have been studied by Simon[3] and Boehm.[4] The condensation is effected in aqueous solution with or without the addition of acid,

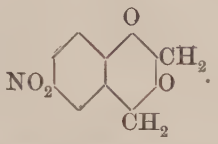
[1] *Trans.*, 1904, **85**, 1225.
[2] *Ber.*, 1904, **37**, 4461.
[3] *Annalen*, 1903, **329**, 30.
[4] *Ibid.*, 269.

With orcinol, to take one example, methylenebisorcinol is formed, and similar products are obtained with derivatives of phloroglucinol.



Methylenebisorcinol.

Busche and Berkhout,[1] working along similar lines and in continuation of former researches, have obtained from *p*-nitrophenol and formaldehyde in presence of dilute sulphuric acid, 5-nitrosaligenin methylene ether :



The nitrocresols and α-nitro-α-naphthol behave in a similar manner. Formaldehyde reacts with hydroxyquinol in presence of sulphuric acid, with the formation of hexahydroxydiphenylmethane,[2]

$$CH_2[C_6H_2(OH)_3]_2.$$

Betti [3] has obtained from β-naphthol and formaldehyde in presence of excess of ammonia a trihydroxynaphthylmethyleneamine having the formula $(OH\cdot C_{10}H_6\cdot CH_2)_3N$, and Blaise and Gault [4] have shown that formaldehyde condenses with 2 molecules of ethyl oxalate in presence of pyridine, giving a substance of the formula

$$CO_2Et\cdot CO\cdot CH(CO_2Et)\cdot CH_2\cdot CH(CO_2Et)\cdot CO\cdot CO_2Et,$$

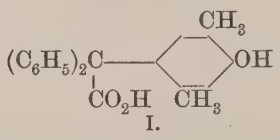
which yields dioxypimelic acid, $CO_2H\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CO_2H$, on hydrolysis. Other interesting cases of condensation with formaldehyde are the production of the compounds $C_5H_4N\cdot CH_2\cdot CH_2\cdot OH$ and $C_5H_4N\cdot CH(CH_2\cdot OH)_2$ from α-picoline, which were originally obtained by Koenigs and Happe,[5] and have been more fully examined by Lipp and Richard.[6]

Tschitschibabin [7] has shown that similar products are obtained from α- and γ-benzylpyridines. Alkylaminobenzaldehydes have been prepared indirectly by the action of formaldehyde on the alkylanilines by Ullmann and Frey.[8]

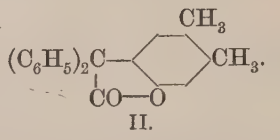
Condensation products of benzilic acid with phenols have been prepared by Geipert,[9] in which the carbinol carbon of the acid attaches

[1] *Annalen*, 1904, **330**, 82.
[2] Liebermann and Lindenbaum, *Ber.*, 1904, **37**, 1171.
[3] *Gazzetta*, 1904, **34**, [i], 212.
[4] *Compt. rend.*, 1904, **139**, 137.
[5] *Ber.*, 1902, **35**, 1343 ; 1903, **36**, 2904.
[6] *Ibid.*, 1904, **37**, 737.
[7] *J. pr. Chem.*, 1904, [ii], **69**, 310.
[8] *Ber.*, 1904, **37**, 1207.
[9] *Ibid.*, 664.

itself to the para- or ortho-position relatively to the hydroxyl group of the phenol; in the one case, parahydroxy-acids are formed (I), and in the other, lactones (II).



I.



II.

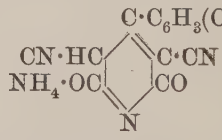
By the condensation of aldehydes with phenols, Liebermann and Lindenbaum,[1] Schreier and Wenzel,[2] and Liebschütz and Wenzel[3] have obtained fluorone derivatives.

From among the many other examples of condensation which have appeared during the current year, the following have been selected.

Moureu[4] has continued his investigations on the condensation of acetylenic esters with alcohol in presence of sodium ethoxide. The product is a mixture of diacetal and the corresponding alkyloxy-ethylene ester. Thus, ethyl phenylpropiolate and sodium ethoxide give $C_6H_5\cdot C(O\cdot C_2H_5)_2\cdot CH_2\cdot CO_2\cdot C_2H_5$ and $C_6H_5\cdot C(O\cdot C_2H_5){:}CH\cdot CO_2\cdot C_2H_5$.

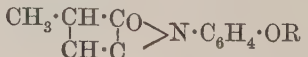
By the action of sodium alkyloxides and phenoxides on acetylene ketones, only the unsaturated alkyloxy- or phenyloxy-ethylene ketone[5] are formed.

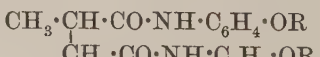
Piccinini[6] finds that aldehydes condense with ethyl cyanoacetate, in presence of ammonia, and yield secondary amides of the formula $RCH(CN)\cdot CO\cdot NH_2$, which on boiling with baryta solution are hydrolysed to substituted malonic esters. In a later paper, he shows that certain aromatic hydroxyaldehydes form γ-substituted dicyanoglutaconimides by this reaction. Vanillin gives the ammonium salt of hydroxy-γ-methoxyphenyldicyanoglutaconimide,



Similar condensation products have been obtained by Issoglio[7] with the nitrobenzaldehydes.

Giffrida and Chimenti[8] have prepared, by condensing pyrotartaric or pyruvic acid with *p*-aminophenols, imides or diamides of the following formula:

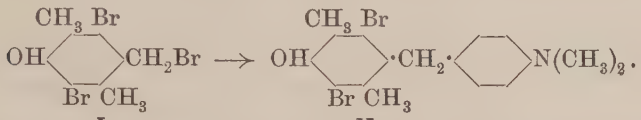




[1] *Ber.*, 1904, **37**, 1171.
[2] *Monatsh.*, 1904, **25**, 311.
[3] *Ibid.*, **25**, 319.
[4] *Compt. rend.*, 1904, **138**, 206.
[5] *Ibid.*, **139**, 208.
[6] *Atti. R. Accad. Sci. Torino*, 1904, **39**, 121.
[7] *Ibid.*, **39**, 140.
[8] *Gazzetta*, 1904, **34**, [ii], 261.

Schoeltz and Huber[1] have obtained a series of condensation products by combining aromatic aldehydes with *p*-aminoacetophenone in an alcoholic solution containing caustic potash. Benzaldehyde gives the compound $C_6H_5 \cdot CH{:}N \cdot C_6H_4 \cdot CO \cdot CH{:}CH \cdot C_6H_5$.

Auwers[2] has shown that the condensation products of pseudophenols and tertiary bases like dimethylaniline, to which he formerly ascribed a different formula, are in reality derivatives of diphenylmethane. The condensation product of pseudocumenol tribromide (I) has the following formula (II):

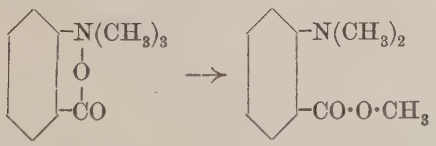


I. II.

It may be observed that the term pseudophenol has been applied to those brominated methyl phenols which contain a mobile bromine atom in the side-chain (in the para-position to the hydroxyl group), and which no longer dissolve in alkalis.

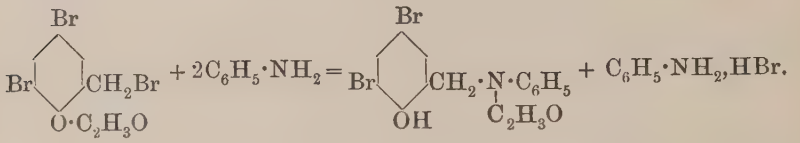
Intramolecular Change.

The clearer views which in recent years have obtained with respect to the phenomenon of dynamic isomerism, wherein the mobility of a hydrogen atom is usually the determining factor, have had the effect of directing more attention to intramolecular changes of all kinds, and to the special conditions which govern them. A molecular change of some interest has been very fully investigated by Willstätter and Kahn[3] in the case of the betaines. They find that the quaternary derivatives of α-, β-, and γ-amino-acids of the aliphatic series exhibit characteristic differences on heating. The α-betaines are converted into esters of tertiary amino-acids, the simplest β-betaine (propiobetaine) isomerises into the trimethylamine salt of acrylic acid, whereas the γ-betaines, like butyrobetaine, decompose into the lactone and trimethylamine. The aromatic betaines, on the other hand, all behave in a similar manner. The *o*-, *m*-, and *p*-betaines of amino-acids are converted on heating into the ester of the dialkylamino-acid thus:

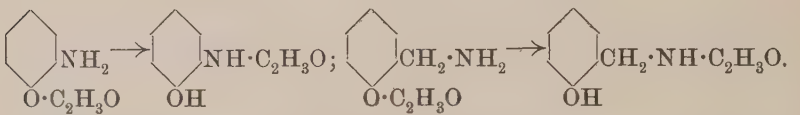


[1] *Ber.*, 1904, **37**, 390. [2] *Annalen*, 1904, **334**, 264.
[3] *Ber.*, 1904, **37**, 401, 1853, 1858.

Another case of molecular change has been observed by Auwers.[1] In the course of experiments on the phenol bromides, Auwers found that by the action of bases on acetyl compounds of the general formula $C_6X_4(O{\cdot}C_2H_3O){\cdot}CH_2Br$, in addition to the replacement of the halogen by the basic substituent, the acetyl group frequently detaches itself from the oxygen and passes to the nitrogen atom. Thus, by the action of aniline on the acetyl derivative of dibromo-*o*-hydroxybenzyl bromide in benzene, dibromo-*o*-hydroxybenzylacetoanilide is formed :



For this reason, the *O*-esters of *o*-aminophenols and *o*-hydroxybenzylamines cannot be isolated, since they isomerise at once into the *N*-esters :



Similar observations on the intramolecular conversion of aminophenylcarbonates have been made by Stieglitz and Upson.[2] Something in the nature of the reversal of the above phenomenon has been investigated by Chattaway and Lewis,[3] who have shown that by heating diacylanilides with hydrochloric acid or zinc chloride, *o*- or *p*-substituted acylaminoketones are produced.

$$C_6H_5{\cdot}N(CO{\cdot}R)_2 \longrightarrow R{\cdot}CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}R.$$

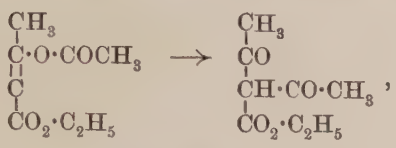
That is, one acyl group passes from the nitrogen atom to the nucleus. A similar process is described by Eijkmann.[4] The acyl phenols, when heated with zinc chloride, are converted into phenolic ketones by the entrance of the acyl group into the nucleus.

In this connection may also be mentioned the interesting intramolecular changes of dimethyldiacetylpyrone which have been studied by Collie.[5]

The mechanism of the conversion which was examined by Claisen,

[1] *Annalen*, 1904. **332**, 159 *et seq.*
[2] *Amer. Chem. J.*, 1903, **31**, 458 ; 1904, **32**, 13.
[3] *Trans.*, 1904, **85**, 386, 589.
[4] *Chemisch Weekblad*, 1904, [i], 453.
[5] *Trans.*, 1904, **85**, 971.

whereby the *O*-acyl derivative of ethyl acetoacetate changes to a *C*-acyl derivative,



has been re-examined by Dieckmann and Stein,[1] who pronounce in favour of Claisen's view that the change is rather inter- than intra-molecular.

Additive Compounds.

It has long been known that many unsaturated compounds lose the property of uniting with bromine. Nef [2] considers that this additive function is determined by the chemical nature of the elements and groups attached to the doubly-linked carbon atoms. Bauer,[3] who has collected a number of facts relating to this question, confirms Nef's views, for he finds that the power of combining with bromine is diminished with the increasing number of carboxyl, ester, phenyl groups, or bromine atoms which are attached to the unsaturated carbon atoms. In certain cases, alkyl groups, when present with the above groups, produce the same effect. Interesting observations of the same nature have been made by Klages [4] on the reduction of substituted styrenes. Sodium and alcohol reduce with difficulty styrene derivatives, having the formulæ $C_6H_5 \cdot CH{:}CR_2$ and $C_6H_5 \cdot CR{:}CR_2$, and it is well known that unsaturated acids like β-dimethylacrylic acid, $(CH_3)_2C{:}CH \cdot CO_2H$, and teraconic acid, $(CH_3)_2C{:}C(CH_2 \cdot CO_2H) \cdot CO_2H$, cannot be reduced at all.

Closely related to the above is the behaviour of the bromine additive compound of unsaturated compounds towards water and alcohol. Hell and Bauer [5] divide the aromatic propylene dibromides into three classes, (1) normal bromides, which, like phenylpropylene and *o*-anethole derivatives, are unaffected by water or alcohol; (2) unstable dibromides, which lose hydrogen bromide and pass into monobrominated propylene compounds like the bromides of diphenyl-, methylphenyl-, and anisylphenyl-propylene, and (3) moderately stable dibromides, which, like *p*-anethole derivatives, can be isolated and with alcohol exchange one bromine for one alkoxyl group.

Many reactions of recent years point to the analogy existing between the additive compounds formed by aldehydes and ketones on the one hand, and by those substances which contain doubly-linked carbon on

[1] *Ber.*, 1904, **37**, 3392.
[2] *Annalen*, 1897, **298**, 208.
[3] *Ber.*, 1904, **37**, 3317.
[4] *Ibid.*, 924, 1721, 2301.
[5] *Ibid.*, 1261.

the other. We refer here more especially to additive compounds with sodium hydrogen sulphite, sulphurous acid, and hydrocyanic acid. Tiemann[1] has collected a number of examples of "hydrosulphonic acid" derivatives of this class and a further contribution to the subject has been recently made by Knoevenagel[2] and his collaborators, who have directed their attention more particularly to $\alpha\beta$-unsaturated ketones containing the group CH:CH·CO. Compounds of this class combine readily with sulphurous acid and sodium hydrogen sulphite, forming hydro-α- or -β-sulphonic acids of the formula

$$-CH_2\cdot CH(SO_3H)\cdot CO- \text{ or } -CH(SO_3H)\cdot CH\cdot CO-.$$

The additive compounds of unsaturated ketones and acids with hydroxylamine have formed the subject of many former communications by Harries and by Posner. A further memoir on the action of hydroxylamine on unsaturated acid esters is contributed by Harries and Haarmann[3] during the current year. Ruhemann and Watson[4] have obtained a series of crystalline additive compounds of olefinic ketones with aromatic amines. To take one example: benzylideneacetylacetone and aniline form a compound of the formula

$$C_6H_5\cdot CH(NH\cdot C_6H_5)\cdot CH(CO\cdot CH_3)_2.$$

Posner[5] has also published a further paper on the combination of mercaptans with unsaturated ketones, which, although too long to abstract, has considerable technical importance.

The formation of additive compounds with hydrocyanic acid has been studied by Lapworth[6] and by Knoevenagel[7] with results of considerable interest.

Lapworth has shown[8] that the presence of small quantities of bases or potassium cyanide hastens the reaction in virtue of the fact that the basic substances diminish the concentration of the hydrogen ions, but increase that of the cyanogen ions.

Additive compounds of azo- and diazo-compounds and quinones with sulphuric acid have been previously described by Hinsberg,[9] and by Hantzsch and Glogauer.[10] Kohler and Reimer[11] have now shown that both aliphatic and aromatic aldehydes, $\alpha\beta$-unsaturated acids and ketones possess the same property.

In a general review of the additive properties of $\alpha\beta$-unsaturated ketones, including his own observations on the additive compounds which they form with hydroxylamine, referred to above, Harries[12] shows that Thiele's theory of partial valencies cannot be entirely

[1] *Ber.*, 1898, **31**, 3297.
[2] *Ibid.*, 1904, **37**, 4038.
[3] *Ibid.*, 252.
[4] *Trans.*, 1904, **85**, 1170.
[5] *Ber.*, 1904, **37**, 502.
[6] *Proc.*, 1904, **20**, 54, 245; *Trans.*, 1904, **85**, 1206, 1214.
[7] *Ber.*, 1904, **37**, 4065.
[8] *Trans.*, 1903, **83**, 997.
[9] *Ber.*, 1894, **27**, 325.
[10] *Ibid.*, 1897, **30**, 2548.
[11] *Amer. Chem. J.*, 1904, **31**, 163.
[12] *Annalen*, 1904, **330**, 185.

reconciled with the known facts. Thiele's theory, it may be stated, is intended to account for the phenomenon so frequently observed during the reduction or bromination of a "conjugated system" (or group containing two adjoining pairs of double bonds, $a=b-c=d$) that the two end atoms only of the chain are capable of entering into union. Thiele supposes that each of the two pairs of atoms is provided with a partial valency in virtue of which the addition is first effected. Moreover, the partial valencies of two adjoining atoms can unite or become "conjugated," leaving thus only the two end atoms free to combine. When this occurs, the bonds between the middle atoms are transposed into an ordinary double bond. The stages in the process may be represented as follows :

$$a=b-c=d \qquad a=b-c=d \qquad ax-b=c-dy.$$

Now Harries finds, contrary to the above view, that unsaturated ketoximes and aldoximes can be reduced to unsaturated amines and that acrolein derivatives can also be converted by the aluminium mercury couple into monohydric alcohols. Similar views have been expressed by Kohler,[1] who points out that, provided the addenda are alike, Thiele's view may hold, but it is otherwise if they are different. Erlenmeyer, jun.,[2] also finds that when cinnamoylformic acid, $C_6H_5\cdot CH{:}CH\cdot CO\cdot CO_2H$, and similar compounds undergo reduction, it is always the ketone group which is attacked, with the formation of $\beta\gamma$-unsaturated hydroxy-acids.

In all these cases, it will be seen, the adjacent and not the end atoms become saturated.

Unsaturated Hydrocarbons.

Few discoveries of recent years have attracted more attention than that of the remarkable series of unsaturated hydrocarbons which Gomberg[3] has isolated by the action of metals (zinc, silver, or mercury) on triphenylchloromethane and analogous compounds. The interest depends, not only on the isolation of hitherto unknown univalent hydrocarbon groups in which carbon is tervalent, but on the curious properties of the new compounds. Various attempts which have been made[4] to bring triphenylmethyl into line with recognised structural formulæ have failed to carry conviction to the discoverer of this compound. In the free state, triphenylmethyl is bimolecular yet distinct from hexaphenylethane, into which, however, it readily polymerises

[1] *Amer. Chem. J.*, 1904, **31**, 243. [2] *Ber.*, 1904, **37**, 1318.

[3] *Ibid.*, 1900, **33**, 3150 ; *Amer. Chem. J.*, 1901, **25**, 317 ; *Ber.*, 1901, **34**, 2726 ; 1902, **35**, 2397 ; 1903, **36**, 376, 3928 ; 1904, **37**, 1626.

[4] Heintschel, *Ber.*, 1903, **36**, 320, 579 ; Tschitschibabin, *ibid.*, 1904, **37**, 4709.

with various catalysts, notably hydrochloric acid. It is unsaturated, combining directly and very readily with oxygen to form a peroxide and with the halogens to form triphenylmethyl halides. It combines, moreover, with ethers and esters, although in these cases it still retains its unsaturated character. Since triphenylmethyl, triphenylmethyl chloride, its double salts with stannic chloride, and the carbinol all dissociate and conduct in liquid sulphur dioxide,[1] it follows that triphenylmethyl possesses the basic properties of a univalent metal, and this view is supported by the fact that the halide compounds form perbromides and periodides.

Triphenylmethyl is a colourless, crystalline solid, but in organic solvents it yields a yellow solution. This change in colour is attributed by Gomberg to the formation of the coloured ion $(C_6H_5)_3C$. The yellow solution of the triphenylhalogenmethane is accounted for in the same way by dissociation into the halogen ion and triphenylmethyl ion from which Gomberg deduces the Rosenstiehl formula for pararosaniline chloride. $(NH_2 \cdot C_6H_4)_3C \cdot Cl$, wherein the colour ion is the basic complex $(NH_2 \cdot C_6H_4)_3C$.

Compounds similar in character to triphenylmethyl have been produced by the action of metals on other triarylchloromethanes. The ditolylphenyl, tritolyl, trinitrotriphenyl, &c., compounds give coloured solutions (the first two being orange and the third greenish-blue) which, on warming, assume a violet, and finally a magenta colour. On cooling, the colour changes occur in the reverse order.

Another unsaturated compound of somewhat remarkable character is that obtained by Thiele [2] in the course of an investigation which had for its object the preparation of the compound $CH_2{:}C_6H_4{:}CH_2$. Although the desired result was not attained, the tetraphenyl derivative, $(C_6H_5)_2C{:}C_6H_4{:}C(C_6H_5)_2$, of this hydrocarbon was prepared. Tetraphenyl-*p*-xylylene is obtained by boiling the bromide, $C_6H_4[CBr(C_6H_5)_2]_2$, with benzene and molecular silver. The new substance crystallises in orange-red needles and the solutions possess a yellow or orange fluorescence.

Hydrocyclic Compounds.

In view of the close relation which subsists between hydroaromatic compounds and many natural products such as are described in a succeeding section (p. 116), the preparation and properties of this group of compounds possess a special interest and importance.

The very large number of synthetical methods which have been announced from time to time do not appear to have exhausted this field of research, and many new reactions have been recently described.

[1] Walden *Ber.*, 1902, **35**, 2018. [2] *Ibid.*, 1904, **37**, 1463.

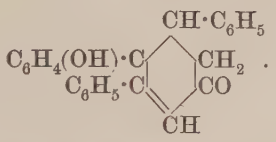
Sabatier and Senderens' method for preparing hydrocyclic alcohols and amines has already been referred to (p. 93).

Lapworth and Chapman[1] and Perkin and Thorpe[2] have shown that ring formation occurs when certain dibasic acids are heated alone or with acetic anhydride. To take one example, the important substance δ-ketohexahydrobenzoic acid (p. 117) is obtained from pentane-αγε-tricarboxylic acid by heating with acetic anhydride:

$$CO_2H\cdot CH\langle \begin{matrix} CH_2\cdot CH_2\cdot CO_2H \\ CH_2\cdot CH_2\cdot CO_2H \end{matrix} =$$

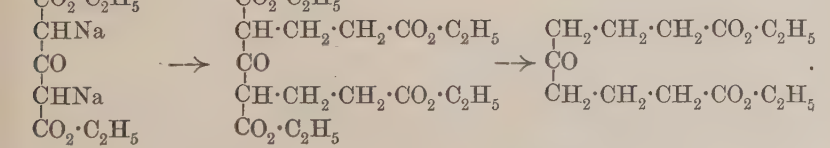
$$CO_2H\cdot CH\langle \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} \rangle CO + CO_2 + H_2O.$$

Garner,[3] some time ago, prepared Δ^2-keto*cyclo*hexene derivatives by condensing benzoin and benzylideneacetone. The reaction has been extended and a variety of hydrocyclic compounds prepared. The compound obtained from benzoin and benzylideneacetone is 3 : 4 : 5-triphenyl-4-hydroxy-Δ^2-keto*cyclo*hexene:



A similar condensation product, triphenyl*cyclo*hexenone, has been described by Wieland,[4] who obtained it from dibenzyl ketone and cinnamaldehyde in presence of diethylamine, and another ketone, diphenylacetone, has been converted by Vorländer and von Liebig[5] into diphenyl*cyclo*pentane.

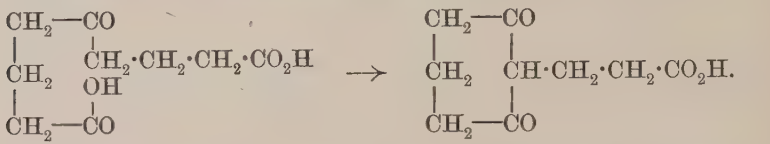
Another synthesis of a hydroaromatic compound is described by von Pechmann and Sedgwick.[6] Acetonedicarboxylic acid (I) condenses with ethyl β-iodopropionate and forms a derivative (II) which breaks up with boiling hydrochloric acid into acetonedipropionic acid (III):



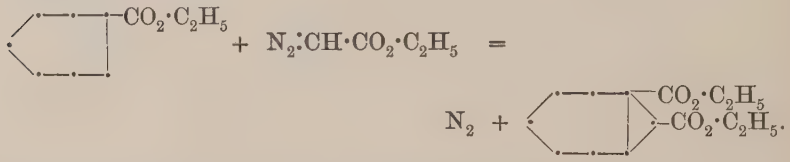
I. II. III.

[1] *Trans.*, 1900, **77**, 464.
[2] *Ibid.*, 1904, **85**, 138, 416.
[3] *Amer. Chem. J.*, 1904, **31**, 143.
[4] *Ber.*, 1904, **37**, 1142.
[5] *Ibid.*, 1133.
[6] *Ibid.*, 3816.

On heating the acid to the melting point, water is removed, and dihydroresorcyl- or diketohexamethylene-propionic acid is produced :

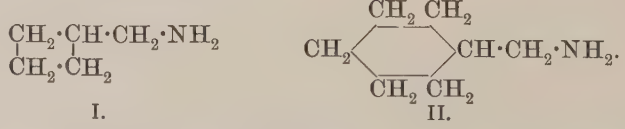


Buchner and Braren [1] have shown that it is possible to prepare a derivative of *cyclo*heptene by the action of ethyl diazoacetate on benzene. The experiments of Buchner and Scheda,[2] undertaken with the view of obtaining an eight-membered carbon ring from ethyl Δ^1-*cyclo*heptenecarboxylate, gave in the first place an oily ester containing a bridged ring of 8 atoms.



Hydrolysis produced a mixture of oily products consisting of unsaturated compounds, from which, after oxidation with permanganate, two isomeric, crystalline acids of the formula $C_8H_{12}(CO_2H)_2$ were isolated, the nature of which has not yet been ascertained.

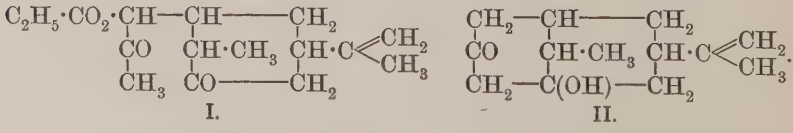
Demjanoff,[3] who succeeded in converting a tetramethyleneamino-compound (I) into a *cyclo*pentene derivative by means of nitrous acid, has now produced a seven-membered ring from a six-membered ring compound (II) in the same way :



I. II.

On treating the hydrochloride of the amine with silver nitrite, suberyl alcohol is formed.

Rabe and Weilinger [4] describe an interesting synthesis of bridged rings from ethyl dihydrocarvonylacetoacetate (I). They find that by intramolecular aldol condensation and the simultaneous removal of carbethoxyl, a dicyclic, ketonic alcohol is produced :



I. II.

[1] *Ber.*, 1900, **33**, 3453 ; 1901, **34**, 982.
[2] *Ibid.*, 1904, **37**, 931.
[3] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 166.
[4] *Ber.*, 1904, **37**, 3816.

The latter has been reduced to the corresponding saturated dicyclic hydrocarbon. Other dicyclic compounds have been prepared by a similar method from methyl*cyclo*hexanone.[1]

Not less important than the synthesis of hydroaromatic compounds is the knowledge of effective means of transforming them into correlated compounds of the aromatic series.

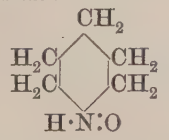
Von Baeyer and others have accomplished it by exhaustive bromination and subsequent reduction of the bromine derivatives, and Markownikoff employs bromine and aluminium bromide whereby aromatic bromine compounds are obtained. Knoevenagel has used bromine alone, and Wallach nitric acid for the same purpose. Interesting results in this connection have been obtained by Crossley [2] and his collaborators. In a recent paper,[3] Crossley has shown that bromine acts on 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene; among other products, 3 : 5-dichloro-*o*-xylene is formed:

$$CMe_2\begin{matrix}<CH{:}CCl\\<CH{\cdot}CCl\end{matrix}>CH \quad \rightarrow \quad CMe\begin{matrix}<CMe{:}CCl\\<CH-CCl\end{matrix}>CH.$$

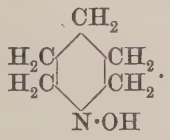
A curious feature of this reaction is the wandering of a methyl group to an adjoining carbon atom such as von Baeyer and Villiger [4] have previously observed in the case of euterpene and *iso*geraniolene.

Heterocyclic Compounds.—Two interesting syntheses of pyridine compounds are recorded during the year, one of chloropyridine from chlorocoumalinic acid, by von Pechmann and Mills,[5] and the other of 2 : 4 : 6-trioxypyridine from ethyl α-cyano-β-iminoglutarate, by Baron, Remfry, and Thorpe.[6]

The action of hydrogen peroxide on piperidine was examined by Wolffenstein some years ago, and he supposed at the time that the product was δ-aminovaleraldehyde. Seeing that the same reagent produced oxyammonium compounds from *N*-alkylpiperidines as well as from secondary aliphatic amines, the original view as to the nature of the oxidation product of piperidine seemed doubtful. Haase and Wolffenstein [7] now bring conclusive evidence to show that the compound is, in reality, a piperidinium oxide or oxime, and is represented by formula I or II:



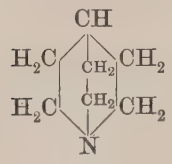
I.



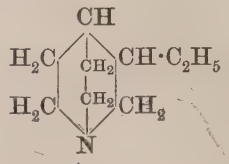
II.

[1] *Ber.*, 1904, **37**, 1671.
[2] *Trans.*, 1902, **81**, 831, 1533; 1903, **83**, 116, 495.
[3] *Ibid.*, 1904, **85**, 264.
[4] *Ber.*, 1898, **31**, 2067; 1899, **32**, 2432.
[5] *Ibid.*, 1904, **37**, 3829.
[6] *Trans.*, 1904, **85**, 1726.
[7] *Ber.*, 1904, **37**, 3228.

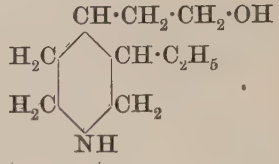
Koenigs[1] has obtained a derivative of quinuclidine (I), which he regards as the possible nucleus of the "second half" of the molecule of the cinchona alkaloids:[2]



I.



II.



III.

The preparation of β-ethylquinuclidine (II) is effected by condensing γ-methyl-β-ethylpyridine with formaldehyde to γ-methylol-methyl-β-ethylpyridine, which is then reduced with sodium and alcohol to methylolhexahydro-β-collidine (III). If the latter is boiled with hydriodic acid and phosphorus, iodine replaces hydroxyl. When the iodine derivative is set free by the cautious addition of caustic soda and taken up with ether, the hydriodide of β-ethylquinuclidine slowly separates from the ethereal solution.

Skraup's quinoline synthesis has undergone several changes since the original method was published. The glycerol has been replaced in turn by glycol and by acetaldehyde and the oxidising agent omitted. The latest modification is the use of amino-compounds with glycerol and arsenic acid proposed by Knüppel.[3] The application of the combined new and old method is the subject of a paper by Bartow and McCollum,[4] and the effect of adding metallic salts and of replacing nitrobenzene by cerium oxide is described by Margosches,[5] but without very definite results.

Both pyridine and quinoline, as Oddo[6] and F. L. Sachs[7] have found, form additive compounds with organomagnesium halides.

It has already been pointed out that Koenigs discovered the property which α- and γ-alkyl-pyridines and -quinolines possess of condensing with formaldehyde. This important reaction has been applied to the preparation of acid derivatives and homologues of quinoline by Koenigs and Mengel,[8] who have examined the condensation of αγ-dimethylquinoline with 1 molecule of formaldehyde. The product is α-ethanollepidine (I), which gives lepidine-α-carboxylic acid on oxidation, and from it lepidine can be obtained by heating:

[1] *Ber.*, 1904, **37**, 3244.

[2] A review of the present position of the chemistry of the alkaloids is contained in a pamphlet by Julius Schmidt, entitled "Die Alkaloidchemie in den Jahren 1900—1904" (F. Enke, Stuttgart).

[3] *Ber.*, 1896, **29**, 1704.

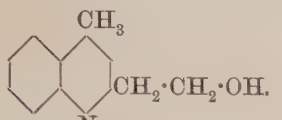
[4] *J. Amer. Chem. Soc.*, 1904, **26**, 700.

[5] *J. pr. Chem.*, 1904, [ii], **70**, 129.

[6] *Atti R. Accad. Lincei*, 1904, **13**, [ii], 100.

[7] *Ber.*, 1904, **37**, 3088.

[8] *Ibid.*, 1322.

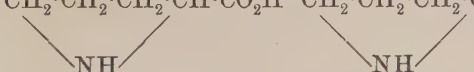


I.

As $\alpha\gamma$-dimethylquinoline by direct oxidation gives lepidine-γ-carboxylic acid, the present method offers a simple means of controlling the course of oxidation. By the introduction of a methylol group into quinaldine and lepidine, they may in a similar way be converted into quinaldinic and cinchoninic acid, an operation which is difficult to effect by any direct method of oxidation. Quinoyl-γ-acrylic acid and its reduction product, the γ-propionic acid, have also been obtained by condensing lepidine with chloral and boiling the chloral-lepidine with caustic potash:

$$C_9H_6N[CH_2\cdot\overset{\gamma}{C}H(OH)\cdot CCl_3] \longrightarrow C_9H_6N(CH{:}\overset{\gamma}{C}H\cdot CO_2H) \longrightarrow C_9H_6N(CH_2\cdot\overset{\gamma}{C}H_2\cdot CO_2H).$$

In the pyrrole and pyrazole group, the synthetical reactions effected by condensation, although numerous enough, offer very little that is intrinsically different from those which have been previously studied by Knorr and others. The reactions consist for the most part in the action of hydrazine and its derivatives on various ketones and ketonic esters. A special interest, however, attaches to α-pyrrolidinecarboxylic acid (I), the presence of which, together with its hydroxy-derivative, has been detected by E. Fischer and others in the products of the hydrolytic decomposition of various proteid substances. It has been synthesised by Willstätter [1] by the action of ammonia on $\alpha\delta$-dibromovaleric acid. Fischer and Suzuki [2] have now prepared in the same way from $\alpha\delta$-dibromovalerylalanine (from the acid chloride and alanine) and ammonia the corresponding pyrrolidine derivative (II). For the first compound Fischer proposes the name "proline" and for the second "prolylalanine":



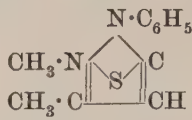
I. Proline. II. Prolylalanine.

Other proline derivatives have been obtained by Fischer and Abderhalden,[3] using similar methods.

A number of new aminopyrazoles have been prepared by Knorr [4]

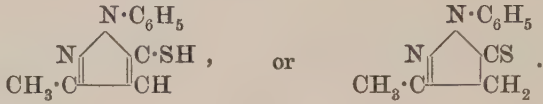
[1] *Ber.*, 1900, **33**, 1160. [2] *Ibid.*, 1904, **37**, 2842.
[3] *Ibid.*, 3071. [4] *Ibid.*, 3520.

from the corresponding acids, and Michaelis[1] has obtained a series of "thiopyrines" or thiopyrazoles. Michaelis' method is to add to an alkali hydrosulphide, into which carbon disulphide vapour has been passed, an aqueous or alcoholic solution of the methyl chloride or iodide of phenylmethylchloropyrazole, or an analogous compound, or to act on antipyrine hydrochloride or similar compound with sodium thiosulphate. Thiopyrine is represented by the following formula:

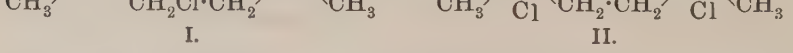


Its physiological action resembles that of antipyrine.

The parent substance of the thiopyrines has also been obtained and has the following structure:

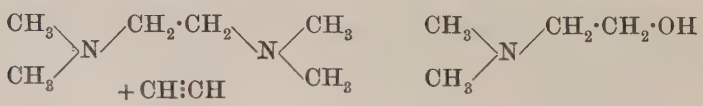


An interesting synthesis of piperazine derivatives by the polymerisation of chloroethylamine and similar compounds is described by Knorr,[2] who finds that chloroethyldimethylamine (I), either free or in aqueous solution, polymerises to dimethylpiperazine hydrochloride (II):



I. II.

The latter decomposes with alkalis into tetramethylethylenediamine (III), ethanoldimethylamine (IV), and acetylene:



III. IV.

The Terpene and Camphor Group.

The most important synthesis of recent years is that of *r*-camphoric acid by Komppa,[3] which, although strictly belonging to the latter part of 1903, is shortly reproduced for reference. Ethyl diketoapo-

[1] *Annalen*, 1904, **331**, 197; *Ber.*, 1904, **37**, 2774.
[2] *Ber.*, 1904, **37**, 3507. [3] *Ibid.*, 1903, **36**, 4332.

camphorate, which is the starting point, was prepared by Komppa by condensing ethyl oxalate with ethyl $\beta\beta$-dimethylglutarate[1]:

$$\begin{array}{l} CO_2R \\ | \\ CO_2R \end{array} + \begin{array}{l} HCH\cdot CO_2R \\ >C(CH_3)_2 \\ HCH\cdot CO_2R \end{array} = \begin{array}{l} CO\cdot CH\cdot CO_2R \\ | \quad >C(CH_3)_2 \\ CO\cdot CH\cdot CO_2R \end{array} + 2R\cdot OH.$$

A methyl group was then introduced by the action of sodium and methyl iodide. This was reduced to the dihydroxy-acid (I), then boiled with hydriodic acid and red phosphorus, and converted into the unsaturated acid (II). The latter combines with hydrobromic acid and forms a bromo-acid (III), and is then reduced with zinc dust and acetic acid to *r*-camphoric acid (IV), which is identical with the product obtained from camphor by oxidation and subsequent racemisation:

$$\begin{array}{l} HO\cdot CH\cdot CH\cdot CO_2H \\ | \quad >C(CH_3)_2 \\ HO\cdot CH\cdot C(CH_3)\cdot CO_2H \end{array}$$

(I) Dihydroxycamphoric acid.

$$\begin{array}{l} CH{=}C\cdot CO_2H \\ | \quad >C(CH_3)_2 \\ CH_2\cdot C(CH_3)\cdot CO_2H \end{array} \quad \text{or} \quad \begin{array}{l} CH\cdot CH\cdot CO_2H \\ \| \quad >C(CH_3)_2 \\ CH\cdot C(CH_3)\cdot CO_2H \end{array}$$

(II) Dehydrocamphoric acid.

$$\begin{array}{l} CHBr\cdot CH\cdot CO_2H \\ | \quad >C(CH_3)_2 \\ CH_2{-}C(CH_3)\cdot CO_2H \end{array}$$

(III) β-Bromocamphoric acid.

$$\begin{array}{l} CH_2\cdot CH\cdot CO_2H \\ | \quad >C(CH_3)_2 \\ CH_2\cdot C(CH_3)\cdot CO_2H \end{array}$$

(IV) *r*-Camphoric acid.

Camphoric acid may be converted into homocamphoric acid[2] by reduction of the anhydride (V) to campholide (VI), which yields cyanocamphoric acid (VII) with potassium cyanide, and, finally, homocamphoric acid on hydrolysis (VIII):

$$C_8H_{14}\begin{array}{l} CO \\ >O \\ CO \end{array} \rightarrow C_8H_{14}\begin{array}{l} CH_2 \\ >O \\ CO \end{array} \rightarrow C_8H_{14}\begin{array}{l} CH_2\cdot CN \\ \\ CO_2H \end{array} \rightarrow$$

V. VI. VII.

$$C_8H_{14}\begin{array}{l} CH_2\cdot CO_2H \\ CO_2H \end{array}$$

VIII.

When the barium salt of homocamphoric acid is distilled, it breaks up into camphor and barium carbonate:

$$C_8H_{14}\begin{array}{l} CH_2\cdot CO\cdot O \\ CO\text{——}O \end{array}>Ba = C_8H_{14}\begin{array}{l} CH_2 \\ | \\ CO \end{array} + BaCO_3.$$

In this way, the complete synthesis of camphor has been effected.

Although Komppa's synthesis has solved the camphor problem as far as its structure is concerned, there remains a large and productive field of research connected with the chemistry of these substances, which is still being carefully cultivated.

[1] *Ber.*, 1901, **34**, 2472. [2] Haller, *Compt. rend.*, 1896, **122**, 446.

The synthesis of what may be termed the fragments of the camphor molecule has formed the subject of several previous communications by W. H. Perkin, jun. During the present year, the same chemist has succeeded in obtaining synthetically *i*-α-campholactone, *i*-α-campholytic acid, and β-campholytic acid (*iso*lauronolic acid).[1] The steps in the process may be briefly described as follows: ethyl cyanoacetate condenses with ethyl bromo*iso*butyrate,

$$CO_2Et\cdot CHNa\cdot CN + CO_2Et\cdot CMe_2Br = \begin{matrix} CO_2Et\cdot CH\cdot CN \\ | \\ CO_2Et\cdot CMe_2 \end{matrix} + NaBr.$$

The sodium compound of this ester reacts with ethyl β-iodopropionate and gives ethyl cyanodimethylbutanetricarboxylate:

$$\begin{matrix} CO_2Et\cdot C(CN)Na \\ | \\ CO_2Et\cdot CMe_2 \end{matrix} + CH_2I\cdot CH_2\cdot CO_2Et = \begin{matrix} CO_2Et\cdot C(CN)\cdot CH_2\cdot CH_2\cdot CO_2Et \\ | \\ CO_2Et\cdot CMe_2 \end{matrix} + NaI.$$

When the latter is boiled with hydrochloric acid, it is hydrolysed and carbon dioxide removed at the same time. The product is α-dimethylbutane-αβδ-tricarboxylic acid. If the dry sodium salt of the acid is heated with acetic anhydride at 140°, a further molecule of carbon dioxide is evolved and inner condensation occurs:

$$CO_2H\cdot CH\langle \begin{matrix} CH_2\cdot CH_2\cdot CO_2H \\ CMe_2 \!\!-\!\!- CO_2H \end{matrix} = CO_2H\cdot CH\langle \begin{matrix} CH_2 \!\!-\!\! CH_2 \\ CMe_2\cdot CO \end{matrix} + CO_2 + H_2O.$$

γ-Keto-ββ-dimethylpentamethylene-α-carboxylic acid.

Methyl and hydroxyl groups are then introduced into the ketone group of the ester by Grignard's method,

$$\begin{matrix} CH_2\cdot CO \\ | \quad | \\ | \quad CMe_2 \\ CH_2\cdot CH\cdot CO_2Et \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot CMe(OMeI) \\ | \quad | \\ | \quad CMe_2 \\ CH_2\cdot CH\cdot CO_2H \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot CMe\!\!-\!\!O \\ | \quad | \quad | \\ | \quad CMe_2 \quad | \\ CH_2\cdot CH\!\!-\!\!CO \end{matrix}.$$

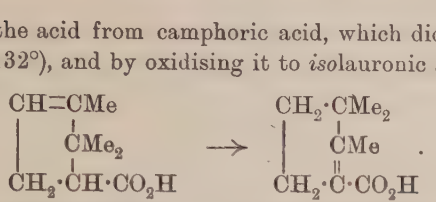
The last product is *i*-α-campholactone. If the lactone is heated with hydrobromic acid, it is transformed into γ-bromotrimethylpentamethylenecarboxylic acid, which with sodium carbonate gives *i*-α-campholytic acid:

$$\begin{matrix} CH_2\cdot CMe\!\!-\!\!O \\ | \quad | \quad | \\ | \quad CMe_2 \quad | \\ CH_2\cdot CH\!\!-\!\!CO \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot CMeBr \\ | \quad | \\ | \quad CMe_2 \\ CH_2\cdot CH\cdot CO_2H \end{matrix} \longrightarrow \begin{matrix} CH\!=\!CMe \\ | \quad | \\ | \quad CMe_2 \\ CH_2\cdot CH\cdot CO_2H \end{matrix}.$$

When digested with dilute sulphuric acid, the α-compound is converted into β-campholytic or *iso*lauronolic acid. The acid was identified by

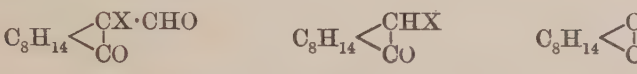
[1] *Trans.*, 1904, **85**, 128.

mixing it with the acid from camphoric acid, which did not affect the melting point (132°), and by oxidising it to *iso*lauronic acid:



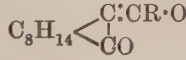
α-Campholytic acid. β- or *iso*-Lauronolic acid.

Several important contributions to the chemistry of halogen and acyl derivatives of camphor and camphorcarboxylic acid have been made by Brühl.[1] It is impossible within the limits of this report to give more than a very incomplete *résumé* of his numerous researches. By brominating and iodating hydroxymethylenecamphor under different conditions, the following halogen derivatives have been obtained (X = Br or I):

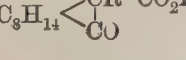


Sodium camphor can be used for the preparation of benzoyl- or formyl-camphor as well as for the alkyl derivatives, in all of which the group attaches itself to the methylene carbon. Brühl finds, on the other hand, that alkyl acetates, acetic anhydride, or acetyl chloride yield mainly *O*-acetyl compounds (I) together with borneol acetate (II):

The preparation of "acetylcamphor" is best effected by means of the magnesium and zinc compounds of bromo- and iodo-camphor by acting on the products with acyl halides and esters. The optical properties of these acylcamphors indicate their derivation from the hydroxymethylene type:



The action of alkyl and acyl chloride and esters, in presence of metals, on camphorcarboxylic acid and its halogen derivatives is the subject of another memoir. If an alkyl halide is added to the sodium compound of ethyl camphorcarboxylate in a non-dissociating medium, like benzene, ligroin, or ether, no action occurs; but alkyl derivatives are obtained if the solvent is methyl or ethyl alcohol. The compounds thus produced have the ketonic form,



[1] *Ber.*, 1904, **37**, 746, 761, 2156, 2163, 2178, 2512, 3943.

Acyl halides, on the other hand, react readily in a non-dissociating as well as in dissociating solvents, and give only enolic compounds :

$$C_8H_{14}\begin{cases}C\cdot CO_2R\\ \|\\ C\cdot OAc\end{cases}.$$

In order to follow the course of these changes, spectrochemical methods (molecular refraction or dispersion) have been adopted. Brühl finds that the production of the sodium compound of the ester in different alcoholic solvents is accompanied by enolisation, and their greater or less reactivity depends on the degree of polymerisation or dissociation. In benzene, for example, the sodium compound has 3—4 times its normal molecular weight, whereas in alcohol it is monomolecular and dissociated. Thus, the alkyl halides seem incapable of reacting with the polymeric form.

Synthesis of Natural Products.

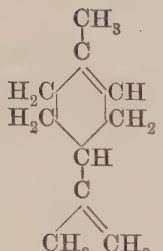
The study of structure with its natural corollary, synthesis, forms so large a part of nearly all organic research and presents so much necessary elaboration in matters of detail, that to attempt to convey an idea of the nature and extent of the current problems in a brief report on the aromatic group is to court certain failure. I propose, therefore, to consider in the present section only such synthetical problems as have received their final solution.

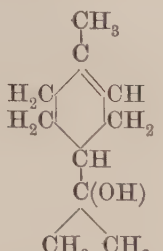
When Komppa's synthesis of camphoric acid, and consequently of camphor (p. 113), had added the last link to that long chain of evidence as to their structure which had been slowly forged by a multitude of skilful workers during years of unremitting study, one chapter in synthetical chemistry was closed. But there remained in the terpene series a long list of allied compounds derived from vegetable sources which as yet included no single member produced by artificial means.

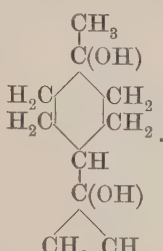
The synthesis of terpin hydrate, terpineol, and dipentene by W. H. Perkin, jun.,[1] may be counted among the brilliant achievements of the year in this field of synthetical chemistry. Both dipentene and terpineol are found in varying quantities in many essential oils. Terpin hydrate, though not strictly a natural product, is closely allied to the other two. Tilden described a convenient method for obtaining terpin hydrate from turpentine as long ago as 1878, and in the following year first prepared terpineol from it. The structural relationship of the three compounds has been established by the joint labours of Wallach, Tiemann, and von Baeyer.

The following are the accepted formulæ of these three compounds :

[1] *Trans.*, 1904, **85**, 654.


Dipentene.


Terpineol.


Terpin.

Perkin's synthesis is effected in the following manner. The starting point is δ-ketohexahydrobenzoic acid, already referred to (p. 107):

$$CO<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H.$$

Its ester reacts readily with magnesium methyl iodide, and the product on hydrolysis yields δ-hydroxyhexahydro-*p* toluic acid,

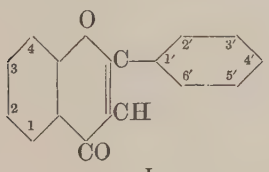
$$MeC(OH)<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H,$$

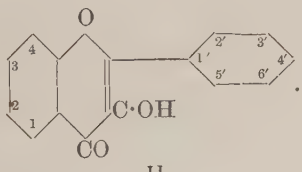
which had already been obtained by Stephan and Heller by the oxidation of $\Delta^{8:9}$-menthenol. This hydroxy-acid dissolves readily in fuming hydrobromic acid, and the solution soon deposits crystals of δ-bromohexahydro-*p*-toluic acid, from which, on treatment with weak alkalis or pyridine, Δ^3-tetrahydro-*p*-toluic acid is obtained:

$$MeC<\begin{matrix}CH{-}CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H.$$

The acid, when converted into the ester and acted on with magnesium methyl iodide, gives terpineol. The latter is transformed, on the one hand, into dipentene by the action of potassium hydrogen sulphate, and, on the other, into terpin hydrate by shaking with dilute sulphuric acid.

Many of the natural yellow dyes have been recognised as belonging to the group of flavone or flavonol derivatives. The flavone (I) and flavonol (II) complexes have the following structure, from which the colouring matters are derived by replacing one or more hydrogen atoms by hydroxyl groups in the numbered rings, and they consequently possess phenolic properties:


I.


II.

The unravelling of the constitution of these substances is due to St. von Kostanecki and his collaborators, and to A. G. Perkin, Herzig, Goldschmidt, and others. In 1898, von Kostanecki succeeded in synthesising the first of the hydroxyflavone dyes, and he has since prepared a large number of similar substances, including the natural products *chrysin* (1 : 3 dihydroxyflavone), from poplar buds; *apigenin* (1 : 3 : 4′-trihydroxyflavone), from parsley; and luteolin (1 : 3 : 3′ : 4′-tetrahydroxyflavone), from weld and dyers' broom. After several unsuccessful trials, the same chemist has at length devised a method for obtaining some of the natural as well as several new flavonol derivatives.

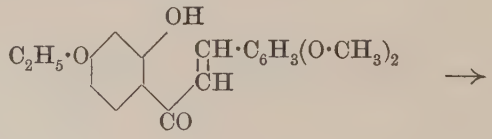
This method may be illustrated in the case of fisetin (3 : 3′ : 4-trihydroxyflavonol), which is the yellow dye of young fustic and yellow cedar.[1] The first step is the preparation of *o*-hydroxychalkone. This is effected by condensing resacetophenone ethyl ether with methylvanillin by means of caustic soda:

$$C_2H_5\cdot O\cdot C_6H_3\langle{}^{OH}_{CO\cdot CH_3} + CHO\cdot C_6H_3(O\cdot CH_3)_2 =$$

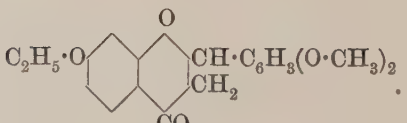
$$C_2H_5\cdot O\cdot C_5H_3\langle{}^{OH}_{CO\cdot CH:CH\cdot C_6H_3(O\cdot CH_3)_2} + H_2O.$$

2-Hydroxy-3 : 4-dimethoxy-4-ethoxychalkone.

On boiling with dilute sulphuric acid, the latter (III) is converted into 3′ : 4′-dimethoxy-3-ethoxyflavonone (IV).



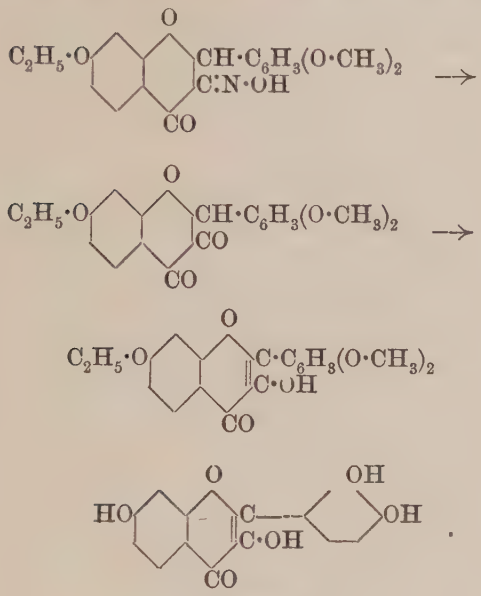
III.



IV.

The flavonone derivative is successively treated with amyl nitrite and hydrochloric acid, which yields an *iso*nitroso-compound; with acetic acid containing 10 per cent. of sulphuric acid, which converts the *iso*nitroso-compound into the corresponding flavonol, and finally with hydriodic acid, which eliminates the alkyl groups and gives fisetin:

[1] *Ber.*, 1904, **37**, 784.



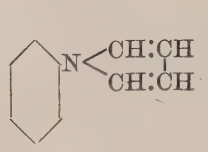
Fisetin.

Quercetin,[1] from quercitron bark, catechu, sumach, &c., kämpferol,[2] from blue larkspur, and galangin,[3] from galanga root, have been synthesised by processes which are merely variations of the above. New methods of synthesis of luteolin[4] and chrysin[5] have also been devised by von Kostanecki.

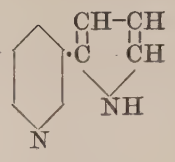
To the steadily growing list of synthesised alkaloids which now includes piperine, coniine, atropine, atropamine, belladonine, *r*-cocaine, tropacocaine, and hyoscyamine, with which the names of Ladenburg and Willstätter are chiefly associated, must be added the principal alkaloid of tobacco, namely, nicotine.

The merit of this new achievement belongs to Pictet and Rotschy.[6] The steps in the discovery are briefly as follows: Pictet and Crepiéux[7] obtained *N*-*β*-pyridylpyrroles (I) by the distillation of *β*-aminopyridine mucate, which isomerises to *αβ*-pyridylpyrrole (II) when its vapour is passed through a red-hot tube. By the action of methyl iodide on the potassium salt of the latter, *αβ*-pyridyl-*N*-methylpyrrolemethiodide (III) is formed. This substance is identical with the methiodide of nicotyrine, obtained by the graduated oxidation of nicotine:

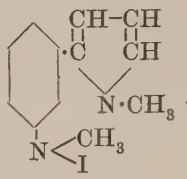
[1] *Ber.*, 1904, **37**, 1402.
[2] *Ibid.*, 2096.
[3] *Ibid.*, 2803.
[4] *Ibid.*, 2625.
[5] *Ibid.*, 3167.
[6] *Ibid.*, 1225.
[7] *Ibid.*, 1895, **28**, 1904.



I.

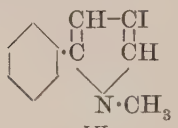


II.

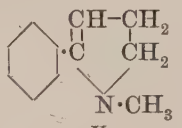


III.

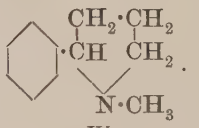
As nicotine contains 4 atoms of hydrogen more than nicotyrine, which may be regarded as its first oxidation product, the next problem was to reduce nicotyrine. This cannot be effected directly; but by the action of iodine and caustic soda on nicotyrine from natural nicotine a crystalline iodine substitution product is obtained (IV) which can be reduced with zinc and hydrochloric acid to dihydronicotyrine (V).[1] The last two hydrogen atoms can be introduced by the reduction of the perbromide of dihydronicotyrine:



IV.



V.



VI.

The new base (VI) appeared to be identical with inactive nicotine. The final problem was how to isolate the artificially-prepared nicotyrine from its methiodide. After several unsuccessful trials it was eventually accomplished by distilling it with lime at as low a temperature as possible. Fifty per cent. of the theoretical yield was thereby obtained. Inactive nicotine was prepared from the product in the manner described above, and then resolved into its active components by crystallising the tartrate. A comparison of *d*- and *l*-nicotines obtained in this way with natural *l*-nicotine is given in the following table. The slight differences in rotation are ascribed by the authors to the hygroscopic character of the bases:

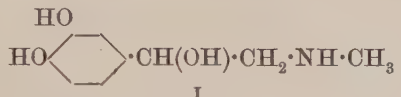
	B. p.	D 10°/4°.	D 20°/4°.	$[\alpha]_D^{20°}$.
Natural *l*-nicotine	246·1—246·2/730·5	1·0180	1·0097	−166·39°
l-Nicotine from the inactive base.	246 —246·5/734·5	1·0177	1·0092	−160·93
d-Nicotine ,, ,,	245·5−246·5/729	1·0171	1·0094	+163·17

The difference in physiological action of the two active nicotines appears at first sight very remarkable, although if we consider the active character of the materials which so largely compose the animal tissues and secretions, it is scarcely surprising that optical isomerides should produce a different effect; for is not the selective fermentation of yeast and other low organisms a manifestation of the same thing? Experiments on guinea-pigs and rabbits show that

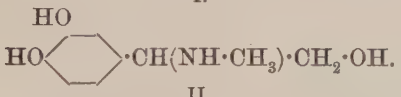
[1] *Ber.*, 1898, **31**, 2018.

the *l*-base is twice as toxic as the *d*-base. Injection of the *l*-base into a guinea-pig produces violent pains and cramp in the extremities; the injection of the *d*-base is painless. Similar differences have been observed in rabbits.

Adrenaline, the active principle of the suprarenal glands, has been the subject of several memoirs which have appeared during the past year, and although the complete synthesis of this important substance is not yet a *fait accompli*, it may be said to have reached its final stage. The structure and properties of adrenaline have been determined by the combined labours of Pauly,[1] Jowett,[2] and Bertrand,[3] resulting in two formulæ, the first of which is preferred by Jowett and the second by Pauly:

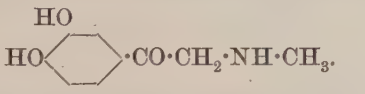


I.

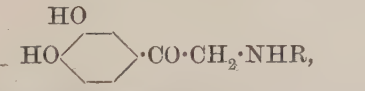


II.

The work of Friedmann [4] seems to confirm the first formula; for he has obtained, by oxidising the optically active tribenzenesulphone derivative of adrenaline, an optically inactive product which is not distinguishable from the tribenzenesulphone derivative of the ketone,



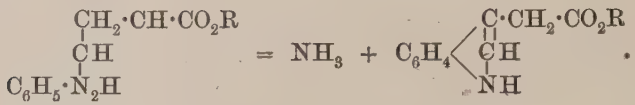
This ketone has been obtained by Stolz [5] by the action of methylamine upon chloroacetylcatechol, and has been shown by Hans Meyer [6] to possess qualitatively the physiological properties of adrenaline in increasing the blood pressure, whilst still more active products were obtained on reduction. Dakin [7] has also obtained a number of bases of the type



several of which are physiologically active. He has also, by reduction of the methylamine base, succeeded in preparing a substance possessing the full physiological activity of adrenaline, although its identity with the natural product is doubtful.

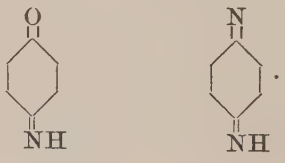
[1] *Ber.*, 1903, **36**, 2944; 1904, **37**, 379.
[2] *Trans.*, 1904, **85**, 192.
[3] *Ann. Inst. Pasteur*, **18**, 672.
[4] *Beitr. chem. Physiol. Path.*, 1904, **6**, 92.
[5] *Ber.*, 1904, **37**, 4149.
[6] *Centralbl. Physiol.*, 1904, **18**, 501.
[7] Private Communication.

Another interesting synthesis of a product of the animal organism is that of indole-acetic acid by Ellinger.[1] The compound is formed by the putrefactive fermentation of tryptophan. Its synthesis is effected by Fischer's method from the phenylhydrazone of the half aldehyde of ethyl succinate :



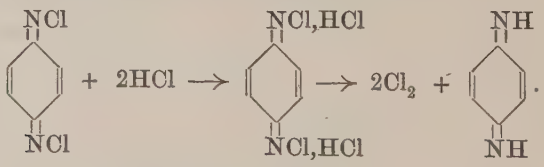
Artificial Dyestuffs.

Since the introduction of Fischer and Nietzki's quinonoid formula into the structure of the triphenylmethane and other dyestuffs, a new stimulus has been given to the study of the constitution of these substances. Among the many investigations which have been pursued during the current year, not the least interesting is that which has led to the discovery by Willstätter, Mayer, and Pfannenstiel [2] of what have been sometimes regarded as the parent substances of many dyes, namely, iminoquinone (I) and di-iminoquinone (II), or the quinoneimines.



I. II.

The method first used was to reduce the well-known quinonedichlorodi-imines with hydrochloric acid in ethereal solution :



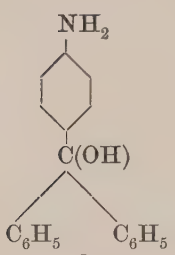
In a later paper, this process is modified, and the mono- as well as the di-imino-compounds were obtained by oxidising *p*-aminophenol and *p*-phenylenediamine by shaking the ethereal solution with dry precipitated silver oxide and anhydrous sodium sulphate. Both compounds are, strange to say, colourless, but become rapidly discoloured in the air and decompose in aqueous solution. The monoimine explodes

[1] *Ber.*, 1904, **37**, 1801. [2] *Ibid.*, 1494, 4605.

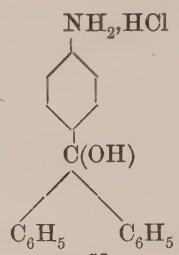
spontaneously in the free state, and is more soluble than the di-imine in ether. It also decomposes in alcohol, has a faint odour of quinone, and colours the skin brown. It forms salts with acids, and with phenol and alkali gives a deep blue solution of indophenol; with dimethyl-aniline and acid, one of phenol-blue. The di-imine does not explode spontaneously like the monimine when heated to the temperature of boiling water, but only by dropping in strong hydrochloric or sulphuric acid. It is a weak base, which forms salts with acids, which are readily decomposed by ammonia. With aromatic amines and phenols, the di-imino-salts produce at once deeply coloured solutions of indamine and indophenol. A passing reference may be made to Willstätter's latest announcement to the effect that catechol can be oxidised with specially prepared silver oxide in dry ethereal solution to *o*-benzoquinone, a substance which has so far eluded every attempt to isolate it.[1] It crystallises in brilliant light red, four- and eight-sided plates, which melt with decomposition at 60—70°, and exhibits a close resemblance to *β*-naphthaquinone in being odourless and non-volatile.

The quinonoid formula of the triphenylmethane colours represents the colour salts as salts of quinoneimines, but with one possible exception—Homolka's colour base of fuchsine—the quinoneimines themselves had not until recently been isolated. Their existence was therefore problematical and their properties were unknown. In a series of memoirs which have been appearing at intervals since 1902, under the somewhat misleading title of "Dibenzalacetone and Triphenylmethane,"[2] von Baeyer and Villiger describe the method of preparing a number of these colour bases, and have sought by this means to establish the structure of the compounds in question on a secure foundation. The question of how far these experiments have fulfilled their purpose scarcely falls within the scope of a report. The first investigation was carried out with *p*-aminotriphenylcarbinol (I). If the ethereal solution of the carbinol is shaken with dilute hydrochloric acid, the orange hydrochloride begins to crystallise. It is regarded as the hydrochloride of the carbinol (II). When this salt is suspended in ether and saturated with hydrogen chloride, it dissolves, and after a time needles of the hydrochloride of the carbinol chloride are deposited (III). The latter salt loses a molecule of hydrogen chloride when heated at 100° in a current of hydrogen, and leaves an orange-red powder, which is distinguished from the carbinol chloride by its solubility in chloroform. It is represented as the hydrochloride of the quinoneimine or colour base (IV), for which von Baeyer proposes the name fuchsonimine:

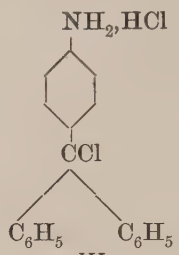
[1] *Ber.*, 1904, **37**, 4744.
[2] *Ibid.*, 1902, **35**, 1189, 3013; 1904, **37**, 597, 2848, 3191.



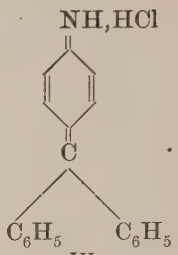
I.



II.

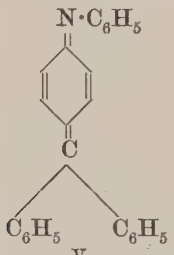


III.

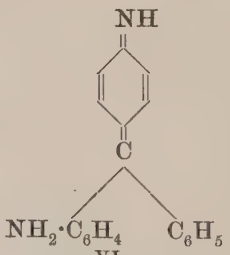


IV.

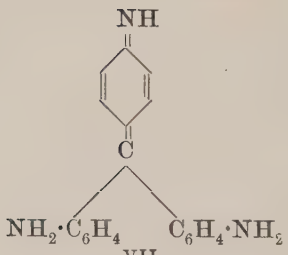
Fuchsonimine itself has not been isolated; for if hydrochloric acid is removed from the hydrochloride (IV) by means of pyridine, it polymerises and gives a dimolecular compound. But the amino- and diamino-derivatives are more stable, and the phenylimino-bases, such as fuchsonphenylamine (V) and the bases of Döbner's violet (VI), fuchsine (VII), and diphenylamine blue (VIII), can be isolated without difficulty:



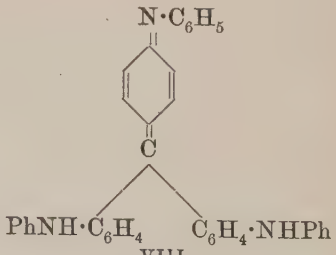
V.
Fuchsonphenylimine.



VI.
Aminofuchsonimine.
(Döbner's violet).



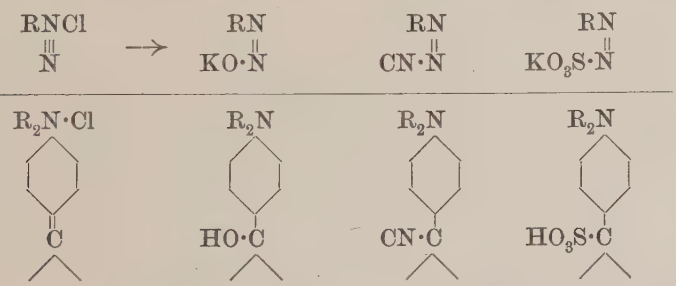
VII.
Diaminofuchsonimine
(Homolka's colour base).



VIII.
Diphenylaminofuchsonphenylamine
(Diphenylamine blue).

The method is to add caustic soda to a solution of the colour salt covered with a layer of ether and to shake the mixture. The base dissolves in the ether and can be separated by evaporating off the solvent. The colour bases have a brown or yellow colour and dissolve in the ordinary indifferent organic solvents. They form colourless carbinols with water, colourless and usually crystalline ethers with alcohol, and

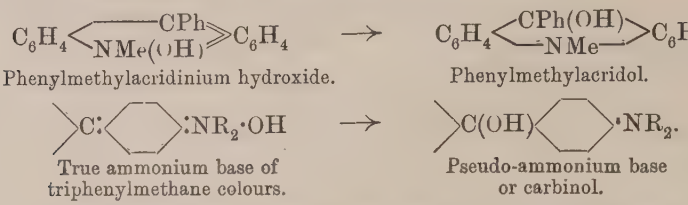
the original coloured salts with acids. No colour bases can be separated from the salts of fully alkylated triaminofuchsonimines like crystal violet, but the action of the alkali is probably to produce the ammonium hydroxide, which changes to the carbinol or pseudo-base, such as Hantzsch has shown to occur with methylacridine and other bases, to which reference will shortly be made. This view is supported by the fact that sodium ethoxide forms with the coloured salt a colourless compound which has been identified as the ether of the carbinol. Von Baeyer and Villiger conclude from the results of their investigation that the usual quinonoid formula of Nietzki is the correct expression of the constitution of the triphenylmethane colours. Without contesting the main conclusions, Hantzsch[1] opposes the view that the colour base of fuchsine and allied colouring matters is an imino-compound. To understand Hantzsch's position, it is necessary to take a short retrospective survey of some of his previous memoirs. By a careful study of the changes which diazonium salts undergo when acted on by solutions of alkalis, alkali cyanides, and sulphites, Hantzsch has formulated the theory that by virtue of the hydroxyl ions the dissociated diazonium hydroxide, which he regards as a true ammonium base, undergoes intramolecular change to the *syn*-diazo-compound or pseudo-ammonium base.[2] The same theory has been applied to account for the colour changes, but more especially changes in electrical conductivity and "abnormal neutrality" of certain coloured salts and salts of colouring matters when alkali, potassium cyanide, sulphurous acid, or a sulphite are added to the solution. Just as the diazonium salts form *syn*-diazotates, diazocyanides, and diazosulphonates, as explained above, so the coloured salts of basic dyes give colourless carbinols, cyanides, and sulphonic acids of the carbinol type :



Evidence of these changes has been derived from the effect produced on phenylmethylacridinium salts and allied compounds, and on salts of triphenyl- and diphenyl-methanes and the azonium group of

[1] *Ber.*, 1904, **37**, 3434.
[2] *Ibid.*, 1899, **32**, 3109, 3132; 1900, **33**, 278.

colours by the addition of an alkali (caustic soda, baryta, or silver oxide). The changes may be represented as follows :



Phenylmethylacridinium hydroxide. Phenylmethylacridol.

True ammonium base of triphenylmethane colours. Pseudo-ammonium base or carbinol.

The base, when first liberated from the salt of the colouring matter, frequently exhibits not only the colour of the original solution, but a strong alkaline reaction and a high conductivity of the order of caustic potash solution. This denotes the presence of the true ammonium base. More or less rapidly the colour fades, the alkalinity vanishes, the conductivity drops, and the insoluble and colourless pseudo-ammonium base is deposited.

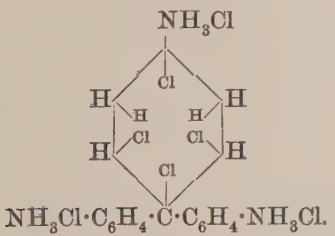
The basis of the colour, according to Hantzsch, is the ammonium ion of the salt or of the hydroxide, and not the imino-colour base of Homolka and its congeners, which from Hantzsch's point of view is an anhydride, bearing the same relation to the true base as gaseous ammonia, NH_3, to ammonium hydroxide, NH_4OH. In support of this view, he points out the striking difference in colour between Homolka's colour base and magenta, and ascribes the magenta colour with which the colour base dissolves in water to the imino-compound uniting with water and becoming, therefore, converted into the partly dissociated ammonium hydroxide. Many independent observations confirm these views. It has been shown, for instance, that just as the solution of a colour salt, after the addition of alkali, may for a time retain its colour, so the reverse operation of adding an acid to a carbinol base may at first produce no coloured solution. Döbner[1] showed that the base of malachite-green dissolves in dilute acid without colour until the solution is heated. Lembrecht and Weil[2] have prepared the colourless oxalate and other salts of malachite-green and allied substances. This colourless oxalate crystallises with 3 molecules of water which are driven off on heating together with the carbinol water, and the metallic green salt is formed. These colourless compounds probably represent undissociated carbinol salts. Similar observations have been made on the behaviour of solutions of the phenolphthaleins and have been explained on similar grounds.[3]

A number of interesting observations on the additive compounds of the rosaniline group have been made by Schmidlin.[4] He finds that

[1] *Annalen*, 1883, **217**, 252. [2] *Ber.*, 1904, **37**, 3058.
[3] Green and Perkin, *Trans.*, 1904, **85**, 398.
[4] *Compt. rend.*, 1904, **138**, 1508, 1709 ; **139**, 506 521, 542, 602.

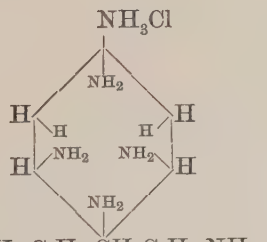
the black trihydrochlorides of pararosaniline and crystal-violet are stable and dissolve with the same colour as the monochloride in water, from which they are again precipitated by alcohol. He finds, moreover, that pararosaniline absorbs at the ordinary temperature and pressure two additional molecules of hydrochloric acid; by lowering the temperature to $-70°$, between 5 and 6 molecules are taken up, and at the temperature of liquid air, 8 molecules are absorbed and the substance is then quite colourless. As the acid escapes at the ordinary temperature, the salt exhibits a series of colour changes, corresponding to the different hydrochlorides, until it reverts to the black trihydrochloride, which, on heating, is further converted into a monohydrochloride. The heptachloride is regarded by Schmidlin as the trihydrochloride of tetrachloro*cyclo*hexanerosaniline (I).

The monohydrochloride, moreover, can absorb ammonia, and by lowering the temperature pararosaniline and crystal-violet will take up 4 molecules of ammonia and become colourless (II). Again, by the hydrolysis of rosaniline salts in acid solutions, 4 molecules of water are added on and a new class of soluble, colourless derivatives, the tetrahydroxy*cyclo*hexane-rosanilines (III), are obtained. The trihydrochlorides of these tetrahydroxy-bases are stable at the ordinary temperature, but lose 4 molecules of water at 50° and pass into the black trihydrochlorides. The author concludes from his researches that the molecule of rosaniline salts contains four aliphatic double bonds, thus confirming with certain modifications, which cannot be discussed here, the quinonoid formula. These compounds are represented by the following structural formulæ:



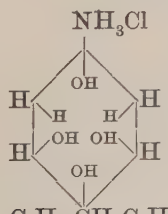
$NH_3Cl \cdot C_6H_4 \cdot C \cdot C_6H_4 \cdot NH_3Cl.$

I.



$NH_2 \cdot C_6H_4 \cdot CH \cdot C_6H_4 \cdot NH_2.$

II.



$NH_3Cl \cdot C_6H_4 \cdot CH \cdot C_6H_4 \cdot NH_3Cl.$

III.

Georgievics[1] has introduced a new formula for the triphenylmethane colours. In the quinonoid formula, only one of the basic groups in the mono-acid salts is united to the acid molecule, and the colour is therefore made dependent on this one group. Now in a solution of crystal-violet a series of colour changes, blue, green, and yellow, each with characteristic absorption bands, is produced by the successive addition of molecular equivalents of acid, and these colours and bands appear to correspond to the neutralisation or removal of the colour effect of successive amino-groups. Thus, the colour and absorption bands of the green solution correspond to those of malachite-green, which contains only two dimethylamino-groups, whilst the yellow colour and its absorption spectrum are the same when produced from crystal-violet by the addition of three, as from malachite-green by the addition of two, molecular equivalents of acid. With more than this amount of acid, the colour of both solutions is discharged. This indicates that each basic group plays a part in the colour effect of the whole molecule, which Georgievics expresses by making each nitrogen atom quinquevalent and linked to its neighbour. The formulæ are not reproduced, as they do not invite serious discussion. As Kaufmann[2] points out, Georgievics has completely ignored the recognised colour effect of the auxochromic group, $N(CH_3)_2$, which E. and O. Fischer years ago found could be neutralised by making the nitrogen quinquevalent either by uniting it with an acid, or transforming it into a quaternary compound by union with an alkyl halide.

Von Braun[3] has attempted to explain the structure of the di- and tri-phenylmethane colours by determining whether the nitrogen of the amino-group functions as a ter- or quinque-valent element. With this object he has employed cyanogen bromide, which has the property of converting the group NR_2 into $N(C{:}N)R$, wherein the nitrogen cannot increase its valency. In derivatives of malachite-green of the formula $(RR'N{\cdot}C_6H_4)_2CPh(OH)$, in which R′ represents (CN), (NO), (CS), (NHPh), the nitrogen exhibits no basic properties, and these compounds dissolve in strong (not in dilute) hydrochloric acid with a red colour. The distinction in colour from that of malachite-green implies, according to this author, a structural difference which is taken to confirm, although the evidence is not quite convincing, the quinonoid structure of the colouring matter.

The coloured compounds which dibenzylideneacetone and triphenylcarbinol give with acids have been the subject of various memoirs by von Baeyer and Villiger,[4] Straus,[5] and Vorländer and Siebert[6] without

[1] *Zeit. Farb. Text. Ind.*, 1904, **3**, 37.
[2] *Ibid.*, 117.
[3] *Ber.*, 1904, **37**, 633, 2670.
[4] *Vide ante*, p. 123.
[5] *Ber.*, 1904, **37**, 3277.
[6] *Ibid.*, 3364.

resulting in anything very definite in regard to their structure. A series of triarylcarbinols has been obtained by Mothwurf [1] and certain hydroxytriphenylcarbinols by Sachs and Thonet,[2] all of which possess the same property of forming coloured salts. The colour reactions with acids of unsaturated hydrocarbons like $\Delta^{1:3}$-dihydrobenzene described by Crossley [3] are significant as indicating how much still remains unexplained of the relations which hold between the colour and the structure of a compound.

Turning from theory to practice, by a survey of the patent lists for the year, one is struck by the fact that side by side with the steady production of new azo-colours there is no diminution in the number of new sulphur dyes. These new dyes, which comprise yellow, orange, brown, blue, violet, black, and also green shades (there is only one red sulphur dye), clearly find favour with the dyer. This is scarcely surprising, for the majority of them are substantive colours, equalling, if not surpassing, in brilliancy and also in fastness to light and soap the fastest of the organic dyes such as indigo, logwood, or aniline black.

The mechanism of the reaction whereby sulphur unites with basic compounds, which was first explained by Bernthsen in the case of methylene blue, and afterwards utilised by Green in the production of primuline, has no doubt prepared the way for Vidal's discovery of the sulphur dyes. Our present ideas about their structure are still very vague and neither the simplicity of the method of production nor the variety of materials which are employed in their manufacture has helped to throw light on the subject. The process consists as a rule in fusing the compound or compounds with sulphur and sodium sulphide at a definite temperature, which may vary considerably in different cases. The materials are usually amino-derivatives of the aromatic series, or nitro-compounds, which, under the action of the sulphide, are reduced to bases.

The leuco-indophenols, the closely allied diphenylamine derivatives and simpler benzene derivatives, like the diamines, amino- and nitro-phenols, which may pass into more complex groups on fusion, are all employed as well as sulphur compounds, such as thiosulphonic acids and thiocarbamides. It seems generally admitted that the nucleus of the colour is a thiazole ring, but more than this cannot yet be affirmed with any certainty.

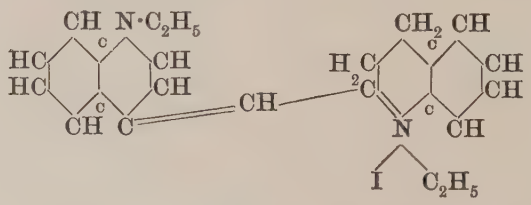
It is interesting to note that Liebermann's well-known "nitroso"-reaction has been turned to account in the production on a manufacturing scale of compounds which have been identified as indophenols,

[1] *Ber*, 1904, **37**, 3153. [2] *Ibid.*, 3327.
[3] *Trans.*, 1904, **85**, 1419.

and which as leuco-compounds can be used for the preparation of sulphur dyes.

The patents which have been applied for in connection with the production of artificial indigo, indoxyl, or indoxylic acid have usually had reference to the method of fusion in attempts to increase the yield. At present, the raw material commonly used in the fusion is either phenylglycine, which is a comparatively cheap product but gives a small yield, or phenylglycine *o*-carboxylic acid, which is more costly, but gives a larger output. Caustic potash, which was originally used, has been replaced wholly or in part by caustic soda, the alkaline earths and sodamide, and even nitrides, alkali carbides, and hydrogenides have been proposed for the purpose.

Numerous patents have also been taken out for the manufacture of halogen derivatives of indigo, colours chiefly of blue and green shades from anthraquinone and yellow acridine colours. A new class of colouring matters which promise to be of some importance has been obtained by König [1] by combining pyridine cyanogen bromide with aromatic amino-compounds. The new colours vary in shade from yellow through orange and red to violet. Besthorn and Ibele [2] also describe a group of new dyes derived from quinoline-α-carboxylic acid. Miethe and Book [3] publish an investigation on the cyanine colours, the technical value of which has greatly increased since their introduction into photo-chemistry and colour photography. The colour called "ethyl red," which is obtained by the action of 2 molecules of quinoline ethiodide on 1 molecule of quinoline ethiodide in presence of caustic potash, has been assigned the following structure:



An ingenious application of colour reactions to physiological investigation is described by Ehrlich and Herter.[4] They find that Witt's β-naphthaquinonesulphonic acid is highly reactive, forming a series of coloured products with aromatic bases as well as with a variety of other substances, including peptone, tyrosine, and uric acid. The compound with dimethyl-*p*-phenylenediaminethiosulphonic acid readily

[1] *J. pr. Chem.*, 1904, [ii], **69**, 105; **70**, 19.
[2] *Ber.*, 1904, **37**, 1236. [3] *Ibid.*, 2008.
[4] *Zeit. physiol. Chem.*, 1904, **41**, 379.

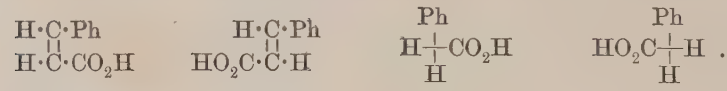
loses sulphurous acid and gives a coloured thiazine derivative. When injected into a rabbit, the skin and other parts assume characteristic colours. Another application of Witt's compound is in detecting the presence of aniline in the body by painting sections of the different organs with a solution of the reagent and observing the colour which develops.

J. B. Cohen.

STEREOCHEMISTRY.

During the past year but few modifications have been suggested in the current views regarding the arrangement of atoms in space; the main activity in this direction has been in connection with the configuration of quinquevalent nitrogen compounds, a subject in which it can scarcely be claimed that any general agreement of opinion has been reached.

E. Erlenmeyer, jun., and A. Arnold have expressed the view[1] that in addition to *cis*- and *trans*-isomerism of the well-recognised fumaroid and maleinoid types a third kind of stereoisomerism is sometimes to be observed; they derive this type theoretically by supposing one of the groups $CR'R''$ in the ethylene derivative, $CR'R'':CR^{i}R^{ii}$, to be rotated at 90° to the other (I or II) so as to give rise to the two enantiomorphously related configurations, III and IV. They consider



I. II. III. IV.

that the plane configurations I and II represent respectively *iso*-cinnamic and cinnamic acids, whilst *allo*cinnamic acid, which forms hemihedral crystals, is the externally compensated mixture having the solid configurations III and IV. P. Pfeiffer has also discussed the apparent discrepancies between the ordinary views as to the configuration of carbon compounds and certain facts relating to the changes of maleinoid and fumaroid compounds.[2] He suggests that the configuration of saturated ethane derivatives is one in which the two ethane carbon atoms occupy the centre of an octahedron, at the six apices of which are situated the six groups attached to the pair of carbon atoms; he thus discards the idea that valency acts in definite directions, and also gives up the ordinary conception of double and triple bonds. The configurations at which Pfeiffer arrives by starting from the above assumption are not very dissimilar from those which Barlow has derived on purely crystallographic grounds, and those which Werner has suggested for explaining the isomerism of many inorganic compounds.

[1] *Annalen*, 1904, **337**, 329. [2] *Zeit. physikal. Chem.*, 1904, **48**, 40.

The question of the primeval origin of optically active substances has been reopened in a new way by A. Byk,[1] who recalls an old experiment of Jamin's, which indicates that terrestrial magnetism causes the partially plane polarised light reflected from such surfaces as that of the ocean to become partially circularly polarised. In the circularly polarised light thus produced, one component—say, *d*-light—predominates on the earth's surface. Byk then confirms the observation of Cotton[2] that *d*-circularly polarised light is differently absorbed by copper ammonium *d*- and *l*-tartrates. The preponderance of *d*-light on the earth's surface must therefore be more favourable to the persistance of one optically active component of racemic acid than to the other.

A result of great interest has been obtained by W. Marckwald[3] in connection with the problem of "asymmetric synthesis." On heating the acid brucine salt of the potentially inactive methylethylmalonic acid, $CMeEt(CO_2H)_2$, until the evolution of carbon dioxide is complete, and liberating the valeric acid thus produced, the latter was found to contain a considerable excess of the *l*-isomeride, $CHMeEt{\cdot}CO_2H$. This is claimed as being the first recorded case of a true "asymmetric synthesis"; to this view, however, Cohen and Patterson have objected that the brucine may separate from the original solution in methylethylmalonic acid with one optically active ion, $CMeEt(CO_2H){\cdot}CO_2^-$, of the latter, and that Marckwald's synthesis should then be regarded merely as an application of one of the three Pasteur methods of resolution. To this objection, Marckwald replies, and apparently effectively, that the whole of the methylethylmalonic acid used was converted into the brucine salt.

In connection with the question of asymmetric synthesis, A. McKenzie shows[4] that on treating menthyl benzoylformate, $PhCO{\cdot}CO{\cdot}O{\cdot}C_{10}H_{19}$, successively with magnesium methyl iodide, water, and acid, a mixture of externally compensated and *l*-phenylmethylglycollic acids, $CMePh(OH){\cdot}CO_2H$, is obtained; the production of an asymmetric carbon atom in the acidic part of the menthyl benzoylformate molecule is so influenced by the presence of the optically active menthyl group that the acidic group becomes optically active. A similar result is obtained on treating menthyl benzoylformate with magnesium ethyl bromide. Further, on reducing *l*-menthyl benzoylformate, slightly more *l*-menthyl *l*-mandelate than *d*-mandelate is produced.

M. A. Ragusin has made the important observation that the distillates from both Russian and American petroleum are lævorotatory;

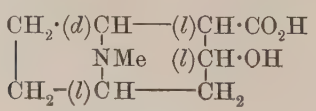
[1] *Ber.*, 1904, **37**, 4696; *Zeit. physikal. Chem.*, 1904, **49**, 641.
[2] *Ann. Chim. Phys.*, 1904, [vii], **8**, 373.
[3] *Ber.*, 1904, **37**, 349.
[4] *Trans.*, 1904, **85**, 1249.

the rotatory powers recorded are small, and the highest values are obtained with the less volatile fractions. These results recall a remark made by P. Walden [1] some years ago to the effect that if optically active petroleums could be found the geological dispute as to the origin of petroleum would be ended; the optical activity seems to indicate that petroleum is necessarily of animal or vegetable origin.

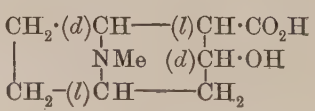
E. Jungfleisch has recorded [2] the results of a number of experiments from which he concludes that *l*-lactic acid undergoes hydrolysis more readily than its enantiomorphously related isomeride. The contradiction of theory thus introduced is perhaps counterbalanced by the observations of A. Piutti [3] that the recorded statement that the crystalline *d*- and *l*-β-asparagines have different densities is erroneous.

A series of determinations of the speed of inversion of cane-sugar by *d*- and *l*-camphorsulphonic acids has been made by R. J. Caldwell [4] with the object of ascertaining whether these enantiomorphously related acids effect the hydrolysis of the optically active sugar at the same or at different speeds. Neither in the case of cane sugar nor of milk sugar could any difference in the speed of hydrolysis be detected.

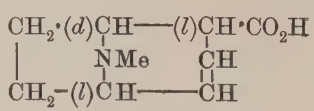
An interesting discussion as to the optical functions of the asymmetric carbon atoms in the closely related alkaloids *l*-ecgonine, *d*-ψ-ecgonine, and anhydroecgonine has been contributed by J. Gadamer and T. Amenomiya; [5] they conclude that the three alkaloids have the following configurations:



l-Ecgonine.



d-ψ-Ecgonine.



Anhydroecgonine.

This result follows mainly because (1) the same anhydroecgonine is produced from both *l*-ecgonine and *d*-ψ-ecgonine, and (2) on subjecting anhydroecgonine to treatment with caustic potash, which converts *l*-ecgonine into *d*-ψ-ecgonine, its optical activity remains unchanged.

During the past year, no methods of a novel character have been devised for resolving externally compensated substances into their enantiomorphously related components. Those variations of the second Pasteur method of resolution which have been introduced during

[1] *Naturwissenschaftliches Rundschau*, 1900, **15**, 15.
[2] *Compt. rend.*, 1904, **139**, 203.
[3] *Gazzetta*, 1904, **34**, [ii], 36.
[4] *Proc. Roy. Soc.*, 1904, **74**, 184.
[5] *Arch. Pharm.*, 1904, **242**, 1.

recent years have, however, been somewhat extended. Thus, McKenzie, continuing his former work with Marckwald [1] on the esterification method of resolving externally compensated acids, shows that when *dl*-mandelic acid is heated with *l*-borneol the residue of unesterified acid contains an excess of the *l*-acid ; [2] the mixture of esters also yields a preponderance of *l*-mandelic acid. This result is interpreted as meaning that *d*-mandelic acid is esterified more rapidly than the *l*-isomeride by *l*-borneol, since the *l*-acid remains unesterified ; the fact that the mixture of esters yields an excess of *l*-mandelic acid on hydrolysis is attributed to the acid, in *l*-bornyl *d*-mandelate, undergoing optical inversion during the formation of the ester more rapidly than is the case with *l*-bornyl *l*-mandelate. On fractionally hydrolysing *l*-bornyl *dl*-mandelate with caustic potash, the first fraction hydrolysed contains an excess of *d*- over *l*-mandelic acid, whilst the last fraction which undergoes hydrolysis gives *dl*- or inactive mandelic acid; *l*-bornyl *d*-mandelate thus appears to be more readily hydrolysed than *l*-bornyl *l*-mandelate, although the latter is the more easily formed.

On hydrolysing *l*-bornyl *dl*-mandelate with more than one equivalent of alcoholic potash, inactive acid is produced ; by treating the ester with much less than one-half an equivalent of potash, *d*-mandelic acid is formed, whilst on using more than one equivalent of caustic potash a salt of *l*-mandelic acid is produced. *l*-Mandelic acid undergoes complete optical inversion when heated with 13 per cent. caustic potash during several hours on the water-bath ; this fact is interesting in connection with the observation of Kipping [3] that *d*-mandelic acid sometimes yields externally compensated phenylchloroacetic chloride with phosphorus pentachloride, and of Easterfield [4] that *l*-mandelic acid gives the same externally compensated acid with fuming hydrochloric acid at 100°. *l*-Menthyl *dl*-mandelate cannot be resolved into its component esters by crystallisation from light petroleum, and is therefore described as partially racemic.

The resolution of externally compensated primary bases by combination with an optically active aldehyde has been further studied by E. Erlenmeyer, jun., and A. Arnold.[5] On condensing *dl-iso*diphenylhydroxyethylamine with *l*-helicin, two substances of the constitution

$$\begin{array}{l} \mathrm{Ph{\cdot}CH{\cdot}OH} \\ \mathrm{Ph{\cdot}CH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_{11}O_5} \end{array}$$

are obtained ; these have $[\alpha]_D$ $-6{\cdot}43°$ and $-43{\cdot}60°$, and on hydrolysis yield *d*- and *l-iso*diphenylhydroxyethylamines having $[\alpha]_D$ $+109{\cdot}72°$ and $-108{\cdot}33°$ respectively in alcoholic solution.

Neville and Pickard [6] have prepared *l*-menthylcarbimide and Forster

[1] *Ber.*, 1899, **32**, 2130.
[2] *Ibid.*, 1904, **37**, 378.
[3] *Trans.*, 1903, **83**, 1005.
[4] *Ibid.*, 1891, **59**, 72.
[5] *Annalen*, 1904, **337**, 307.
[6] *Trans.*, 1904, **85**, 685.

and Atwell's *d*-bornylcarbimide; they suggest the application of these two substances to the resolution of externally compensated hydroxy-compounds and bases. Forster and Atwell, however, indicate[1] that bornylcarbimide reacts too sluggishly with hydroxy- and amino-compounds to render it useful in the suggested connection. The writer may perhaps be allowed to point out that *d*-butylcarbimide, which forms the main constituent of oil of spoonwort, could certainly be substituted with success for the bornyl- and menthyl-carbimides mentioned above.

A number of externally compensated acids have been resolved into their optically active components during the past year. A new method for resolving fermentation lactic acid has been devised by E. Jungfleisch[2] depending on the crystallisation of the quinine salt under special conditions; although the carrying out of the new method suggests several points of theoretical interest, it does not appear to offer any advantages over the method devised by Purdie and Walker.[3]

Morrell and Bellars[4] have resolved β-methylglyceric acid,

$$CHMe(OH)\cdot CH(OH)\cdot CO_2H,$$

by crystallisation with quinidine; the salt *l*-B *l*-A is the least soluble in water, and the crystalline *l*-acid separated therefrom gives $[\alpha]_D$ −13·51° in aqueous solution. The salt *l*-B *d*-A could not be obtained in a pure state, but by applying the fact that the barium salt of the inactive acid is insoluble in alcohol, whilst that of the active acid is somewhat soluble, the pure barium salt of the *d*-acid was isolated.

Externally compensated *p*-methoxymandelic acid can be readily resolved into its *d*- and *l*-components ($[\alpha]_D$, in water, +146·1° and −146·2°) by crystallisation with cinchonine;[5] the specific rotatory powers are but slightly less than that of mandelic acid ($[\alpha]_D$ + or −156·4°).

H. B. Hill and F. W. Russe[6] have also resolved β-dihydrofurfurane-αα′-dicarboxylic acid by the crystallisation of its cinchonine salts; in one-half per cent. aqueous solutions, the acids have the specific rotatory powers of + or − 500°. Owing to the possibility of this resolution, the authors are able to prove that the β-dihydro-acid is externally compensated, and that the so-called α-acid is the potentially inactive isomeride.

Phenyl*iso*paraconic acid has been resolved by crystallisation with strychnine;[7] the optical antipodes give $[\alpha]_D$ + 14·72° and − 14·51° in

[1] *Trans.*, 1904, **85**, 1188.
[2] *Compt. rend.*, 1904, **139**, 56.
[3] *Trans.*, 1895, **67**, 616.
[4] *Ibid.*, 1904, **85**, 197.
[5] E. Knorr, *Ber.*, 1904, **37**, 3172.
[6] *Ber.*, 1904, **37**, 2538.
[7] R. Fittig and P. Jehl, *Annalen*, 1904, **330**, 292.

alcoholic solution, whilst in acetic acid solutions the signs of the rotatory powers are reversed. *Penicillium glaucum* destroys the *l*-acid more rapidly than its isomeride, so that the latter can be readily isolated by aid of the mould. Phenylparaconic acid,

$$\begin{array}{l} \mathrm{Ph{\cdot}CH{-}CH{\cdot}CO_2H} \\ \quad\vert\quad\quad >\mathrm{CH_2} \\ \mathrm{O{-}{-}CO} \end{array},$$

has also been resolved by crystallisation with strychnine; the component acids give $[\alpha]_D$ + 64·33° and − 65·33° in alcoholic solution.

C. Neuberg and M. Silbermann[1] have set at rest the doubts which prevailed as to the optical constants of the *d*- and *l*-glyceric acids $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, by resolving the externally compensated acid by crystallisation with brucine; brucine *l*-glycerate separates as the least soluble salt, and from it barium *l*-glycerate of $[\alpha]_D$ − 17·34° was obtained. The barium *d*-glycerate from *d*-glucuronic acid gave $[\alpha]_D$ + 17·1°.

E. E. Blaise and L. Marcilly[2] state that *aa*-methylethylhydracrylic acid, $OH{\cdot}CH_2{\cdot}CMeEt{\cdot}CO_2H$, cannot be resolved into its optically active components by crystallisation with quinine or cinchonine.

S. Condelli[3] finds that the optimum temperature for the decomposition of racemic acid by *Aspergillus niger* is 35°; he shows that *d*-tartaric acid is most readily destroyed by the organism at low temperatures, whilst the *l*-isomeride is the more readily attacked at higher temperatures.

A. Pictet and A. Rotschy,[4] having prepared synthetically tetrahydronicotyrine and shown it to be identical in constitution with nicotine of natural origin, resolved it into its optically active components by crystallisation with *d*-tartaric acid. The salt *l*-B *d*-A is the least soluble, and from it *l*-nicotine ($[\alpha]_D$ − 160·93°), identical with the naturally occurring alkaloid ($[\alpha]_D$ − 166·39°), is separated. The hitherto unknown enantiomorphously related isomeride, *d*-nicotine ($[\alpha]_D$ + 163·17°), was also isolated. Physiological experiments made with the two isomerides lead to the interesting result that *l*-nicotine is about twice as poisonous as *d*-nicotine; the injection of the *l*-base is extremely painful to the animal, whilst that of the *d*-isomeride seems to cause no pain.

Optically active homologues of benzene have been prepared by A. Klages and R. Sautter.[5] Magnesium *d*-amyl iodide acts on benzaldehyde yielding *d* hexenylbenzene, $CHPh{:}CH{\cdot}CHMeEt$ ($[\alpha]_D$ + 50·3°), which, on reduction, gives *d*-hexylbenzene, $CH_2Ph{\cdot}CH_2{\cdot}CHMeEt$

[1] *Ber.*, 1904, **37**, 339.
[2] *Bull. Soc. chim.*, 1904, [iii], **31**, 317.
[3] *Gazzetta*, 1904, **34**, 86.
[4] *Ber.*, 1904, **37**, 1225.
[5] *Ibid.*, 649.

($[\alpha]_D + 17{\cdot}2°$); the latter substance could not be caused to undergo optical inversion. The authors found difficulty in preparing *d*-amyl alcohol by the method of Marckwald and McKenzie, and the former has therefore[1] given further directions for applying the method. He also remarks that the difficulty of preparing pure *d*-amyl alcohol is partly due to the interesting fact that all the known crystalline derivatives of *d*-amyl and *iso*amyl alcohols form solid solutions; thinking that this tendency towards the formation of solid solutions might be sufficiently diminished if large substituting groups were introduced into the molecules of the mixture of alcohols, he has prepared the urethanes. *iso*Amylurethane and *d*-amylurethane, however, still form solid solutions, although the tendency to do so is less than with the previously investigated solid *iso*- and *d*-amyl compounds. Thus the *d*-urethane is insoluble in the *iso*-compound, but the *iso*urethane is fairly soluble in the *d*-isomeride; the two isomerides therefore cannot be separated by fractional crystallisation.

Marckwald finds that the solubility curve of mixtures of the barium salts of *d*-amyl- and *iso*amyl-sulphuric acids is quite continuous, and has found an analytical expression representing the curve. He also gives a good method of preparing *d*-valeric acid ($[\alpha]_D + 8{\cdot}75°$) by the oxidation of *d*-amyl alcohol with chromic acid, and has prepared pure *d*-amyl iodide ($[\alpha]_D + 5{\cdot}64°$) and bromide ($[\alpha]_D + 3{\cdot}68°$). *d*-Amylamine ($[\alpha]_D - 5{\cdot}86°$), prepared from *d*-amylphthalimide, is remarkable in that its hydrochloride is optically inactive to sodium light. Marckwald has also prepared the simplest possible optically active paraffin, namely, *d*-methylethylpropylmethane, CHMeEtPr, in a pure state ($[\alpha]_D + 9{\cdot}5°$) by the interaction of *d*-amyl iodide, ethyl iodide, and sodium.

W. Meyerhoffer discusses[2] the equilibrium conditions attending the separation of the components of an externally compensated acid by Pasteur's method of crystallisation with an optically active base. Since, in such a crystallisation, three salts are capable of formation, namely, the salts, *d*-B *d*-A, *d*-B *l*-A, and the partially racemic salt, 2*d*-B *dl*-A, there should be three ranges of temperature distinguishable, corresponding with the separation from the solution, side by side, of the two solid salts, (a) *d* B *d*-A, and *d*-B *l*-A, (b) of the less soluble of the two latter and the partially racemic salt, and (c) of the partially racemic salt alone.

Power and Tutin[3] have separated a *l*-quercitol,

$$OH{\cdot}CH\begin{matrix}<\\ \end{matrix}\begin{matrix}CH(OH){\cdot}CH(OH)\\ CH(OH){\cdot}CH(OH)\end{matrix}\begin{matrix}>\\ \end{matrix}CH_2,$$

having $[\alpha]_D - 73{\cdot}9°$, from the leaves of *Gymnema sylvestre*. Eight optically active isomerides of this constitution should exist, and the

[1] *Ber.*, 1904, **37** 1038. [2] *Ibid.*, 2604. [3] *Trans.*, 1904, **85**, 624.

one now described is not enantiomorphously related to the *d*-quercitol already known, because this has $[\alpha]_D$ +24·16°. The two sugars fucose and rhodeose have been shown to be enantiomorphously related by E. Voto ek [1]

A good deal of work has been done on the actual determination of rotatory powers and on the deductions to be drawn therefrom. A. Rosenheim and H. Aron find that the rotatory power of *d*-tartaric acid is quadrupled by addition of a caustic potash solution of stannic chloride, and attribute this to the formation of a complex acid ion containing tin and the tartaric acid radicle; the stannitartrates thus formed were isolated by Henderson, Orr, and Whitehead.[2] H. Grossmann and H. Pötter have examined [3] the effect of change of temperature on the rotatory powers of ammonium molybdanylbimalate, $MoO_2(C_4H_5O_5 \cdot NH_4)_2$, in aqueous solution. In 3—12 per cent. solutions of malic acid to which the corresponding amount of ammonium molybdate has been added, the specific rotatory power attains a maximum value at 35°; above and below that temperature, the rotatory power diminishes. The same kind of change of rotatory power until a maximum value is reached during continous rise of temperature has been previously observed to occur by P. F. Frankland and F. M. Wharton in the case of diethyl dibenzoyltartrate.[4]

Patterson has determined [5] the rotatory powers of methyl, ethyl, and *n*-propyl *d*-tartrates at temperatures from 10—100°, and finds that the comparison of the data at the same temperatures indicates but little relationship. By extrapolation, however, it is shown that the esters should be optically inactive for the D-line at 0°, − 34°, and − 60° respectively, and it is suggested that these are "corresponding temperatures" for the optical properties of the substances. Generally, also, the temperatures T°, T° − 34°, and T° − 60°, are corresponding temperatures for the three esters, T° being the temperature on the absolute scale. This view is supported by the result that the ratios of the molecular rotatory powers of the esters are nearly constant at corresponding temperatures. At corresponding temperatures, the ethyl *d*-tartrate gives $[M]_D$ about 2·1 times that of the methyl ester, and the $[M]_D$ of *n*-propyl tartrate is 1·41 times that of the ethyl salt.

The same worker has also [6] contributed a mass of valuable experimental data including values of the rotatory powers of sodium tartrate, potassium tartrate, potassium methyl tartrate, potassium ethyl tartrate, potassium *n*-propyl tartrate, and of methyl, ethyl, and *n*-propyl tartrates in aqueous solutions at series of temperatures between 10° and 100°, and values of the molecular solution volumes

[1] *Ber.*, 1904, **37**, 2859.
[2] *Trans.*, 1899, **75**, 555.
[3] *Ber.*, 1904, **37**, 84.
[4] *Trans.*, 1896, **69**, 1583.
[5] *Ibid.*, 1904 **85**, 765.
[6] *Ibid.*, 1116 and 1153.

of methyl, ethyl, *n*-propyl, potassium methyl, potassium ethyl, and potassium *n*-propyl tartrates. A distinct connection is shown to exist between the gram-molecular contractions on solution and the change in molecular rotatory power set up by such solution. The rotatory powers of the alkyl tartrates are increased by solution in water, and a rapid diminution occurs on heating the dilute solution; in the solvent-free state, the rotatory powers of the esters increase as the temperature rises.

P. F. Frankland and J. Harger have studied [1] the rotatory powers of the methyl and ethyl esters of the di-*o*-, -*m*-, and -*p*-nitrobenzoyltartaric acids at temperatures between 15° and 180°. The introduction of nitro-groups into the dibenzoyltartrates in para- or meta-positions greatly increases the molecular rotatory power; the introduction of nitro-groups into the ortho-position diminishes the molecular rotatory power above 130°, but as the temperature falls the rotatory power increases so rapidly that ethyl *o*-nitrobenzoyltartrate has a higher rotatory power at 15° than has its para-isomeride.

The rotatory powers and dispersions have been determined by E. Wassmer and P. A. Guye [2] of a large number of acidic derivatives of ethyl malate. In this series, the specific rotatory power diminishes continuously whilst passing from ethyl propionylmalate to ethyl decoylmalate, but the molecular rotatory power attains a maximum in ethyl butyrylmalate. A number of alkyl lactates were also examined, and in the latter series the specific rotatory power attains a maximum value in octyl lactate.

As a supplement to the work of Briggs and Cohen [3] on the *l*-menthyl esters of the six dichlorobenzoic acids, J. B. Cohen and H. S. Raper have examined the *l*-menthyl esters of the ten chlorobromobenzoic acids. The values of $[M]_D$ for the corresponding chlorobromo- and the dichloro-esters are of the same order of magnitude. The molecular rotatory power of *l*-menthyl benzoate ($[M]_D$ −236·3°) decreases most when the substituting halogen atoms are ortho- to the carboxyl group, and decreases least when the halogen atoms are meta- to the carboxyl. The rotatory powers of the *l*-menthyl *o*-, *m*-, and *p*-iodobenzoates ($[M]_D$ −246°, −234·5°, and −241·2° respectively) are not in the same order as those of the corresponding chloro- and bromo-benzoates given by Cohen and Briggs (*loc. cit.*) and by Tschugaeff.[4]

W. Urban,[5] has prepared and determined the rotatory powers of a long series of alkylated *d*-butylthiocarbamides and *d*-butylcarbamides by the action of primary and secondary amines on *d*-butylthiocarb-

[1] *Trans.*, 1904, **85**, 1571.
[2] *J. Chim. phys.*, 1903, **1**, 257.
[3] *Trans.*, 1903, **83**, 1213.
[4] *Abstr.*, 1903, **84**, ii, 2.
[5] *Arch. Pharm.*, 1904, **242**, 51.

imide, CS:N·CHMeEt. The substances examined were of the types NHR·CS·NH·CHMeEt, NR_2·CS·NH·CHMeEt, and

R:N·CS·NH·CHMeEt,

and the corresponding types in which sulphur is replaced by oxygen. In spite of the large changes which are caused throughout the series in the mass of the group attached to the butyl radicle, the molecular rotatory powers do not differ greatly; large variations in the rotatory power attend the change of solvent from alcohol to chloroform.

J. W. Walker found[1] that the complete hydrolysis of amygdalinic acid yields externally compensated mandelic acid; H. D. Dakin now shows[2] that, on fractional hydrolysis with baryta, *d* mandelic acid is first liberated, whilst *l*-mandelic acid preponderates in the hydrolysis product of the final fraction. Amygdalin is a maltoside of *l*-mandelic acid, and on partial hydrolysis yields amygdalinic acid, which is a mixed glucoside of *d*- and *l*-mandelic acids. By agitating amygdalin with baryta solution, Dakin has converted it into an isomeride, *iso*amygdalin ($[\alpha]_D$ – 47·6°), which yields both *d*- and *l*-mandelic acids on complete hydrolysis. Walker had previously suggested that some such partially racemic substance as this is an intermediate product in the conversion of amygdalin into amygdalinic acid.

Bowack and Lapworth[3] find that *l*-menthyl cyanoacetate,

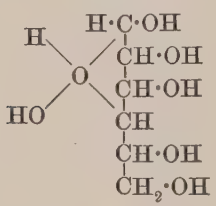
$C_{10}H_{19}O·CO·CH_2·CN$,

and several of its derivatives do not exhibit mutarotation; the specific rotatory power of these substances does not afford evidence of changing molecular structure, although such evidence is found in the mutarotation of derivatives of *l*-menthyl acetoacetate.[4] Only slight mutarotation was observed by Hann and Lapworth[5] to occur amongst the *l*-menthyl alkylideneacetoacetates.

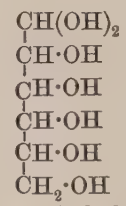
Lowry has shown[6] that the equilibrium proportion in which two dynamic isomerides exist in a solution may be ascertained by saturating a solvent with the stable form, and at once determining how much (a) has gone into solution, then allowing the solution to remain in contact with the stable form until equilibrium has been established between the dynamic isomerides present in the solution, and again determining the composition (b) of the solution; the ratio $a/(b-a)$ represents approximately the proportion in which the isomerides are present in the equilibrium solution. In the case of solutions of nitro- and π-bromo-camphors, the normal and ψ-forms are in equilibrium when present in the solution in the ratio 5 : 1 approximately. On applying a similar method to glucose and galactose, Lowry found[7] that the

[1] *Trans.*, 1903, **83**, 472.
[2] *Ibid.*, 1904, **85**, 1512.
[3] *Ibid.*, 42.
[4] *Ibid.*, 1903, **83**, 1117.
[5] *Ibid.*, 1904, **85**, 49.
[6] *Ibid.*, 1541.
[7] *Ibid.*, 1551.

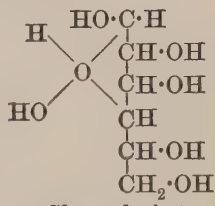
proportion of α-sugar present in the equilibrium solution decreases as the amount of water in the solvent increases; thus in methyl-alcoholic solution one-half of the sugar is present as the α-form, whilst in the mixture $EtOH,H_2O$, only 40 per cent. is of the α-form. It is suggested that the α- and β-forms are present in about equal proportion in the solutions, but that in the aqueous solutions a third hydrated and intermediate form is produced, thus:



α-Glucose hydrate.



Glucose aldehydrol.



β-Glucose hydrate.

E. F. Armstrong and Arup[1] have made careful determinations of the velocities of hydrolysis of α- and β-glucose pentacetates, β-galactose pentacetate, and sucrose pentacetate by potash. The results obtained are very concordant, and indicate that the velocity and course of the hydrolysis of α- and β-glucose acetates are identical, but that galactose pentacetate hydrolyses considerably more rapidly. The values obtained for octacetylsucrose are of peculiar interest, in that they indicate no distinction between the behaviour of the acetyl groups in the sucrose derivative and the glucose from which it is derived. The velocity coefficient in each case diminishes as the time increases, indicating that the acetyl groups do not all separate at the same rate. Determinations of the velocity of hydrolysis of the tetracetates of α- and β-methyl-glucosides and of α- and β-methylgalactosides show that all four substances are hydrolysed at the same rate; this is important, in view of the fact that in these isomerides the acetyl groups occupy similar positions in the molecules. The interconversion of the *d*-glucose α- and β-pentacetates has been studied by C. L. Jungius.[2]

T. Purdie and J. C. Irvine have shown[3] that on methylating tetramethylglucose, tetramethyl-β-methylglucoside (m. p. 42—43°; $[\alpha]_D$, in water, −11·6°) is the main product, a liquid stereoisomeric tetramethyl-α-methylglucoside ($[\alpha]_D$, in water, +147·4°) being formed in small quantity. The β-glucoside contrasts with the α-isomeride in its more rapid hydrolysis with acid and by being hydrolysed by emulsin.

Tetramethylglucose exhibits mutarotation; the α-form (m. p. 88—89°; $[\alpha]_D$ +100·8°) is produced by repeated crystallisation from petroleum,

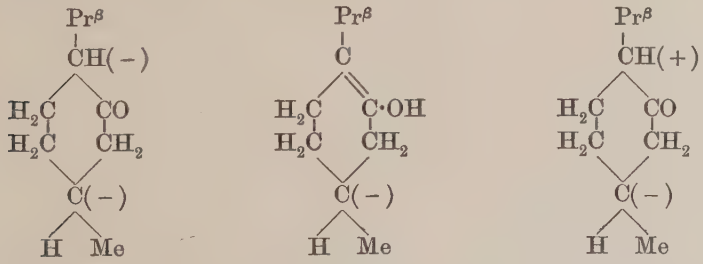
[1] *Trans.*, 1904, **85**, 1043.
[2] *Proc. K. Akad. Wetensch. Amsterdam*, 1904, **6**, 779.
[3] *Trans.*, 1904, **85**, 1049.

and on heating above its melting point yields the β-form ($[\alpha]_D$ +73·1°), which on preservation reverts to the α-modification. The form stable in solution ($[\alpha]_D$ + 83·3°) appears to be an equilibrium mixture of the two. Since mutarotation is also observed in benzene and carbon tetrachloride solutions, the assumption of ionisation or the formation of hydrates is not essential for explaining the phenomena.

R. Behrend and P. Roth have observed also that *d*-glucose shows[1] mutarotation in pyridine solutions, and state that the specific rotatory power of *d*-glucose in pyridine is at first $[\alpha]_D$ + 138·88°, but that during the lapse of 24 hours this value falls to +71·17°; they conclude that this fact excludes the possibility of the mutarotation being due to the formation of hydrates.

J. C. Irvine and A. Cameron[2] obtain a liquid tetramethyl-α-methylgalactoside ($[\alpha]_D$, in water, +143·4°) by the silver oxide method of alkylating α-methylgalactoside; on hydrolysis with hydrochloric acid, it yields a liquid tetramethylgalactose, which exhibits mutarotation in aqueous, alcoholic, and benzene solutions. On methylation, tetramethylgalactose yields stereoisomeric tetramethyl-α- and -β methylgalactosides; the α-isomeride is the main product when methyl alcohol and hydrogen chloride are the methylating agents, whilst alkylation with silver oxide and methyl iodide gives mainly the β-isomeride. The latter is crystalline (m. p. 44—45°) and is more readily hydrolysed than the α-isomeride with dilute acids or emulsin.

Tutin and Kipping[3] demonstrate the probability that the so-called *d*- and *l*-menthones produced from menthol are stereoisomeric, but not enantiomorphously related. They are interconvertible by passage through an enolic form, thus:



l-Menthone. Enolic form. *d*-Menthone or *l*-*iso*menthone.

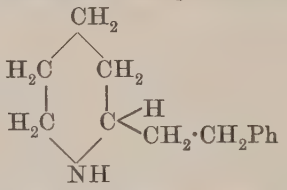
From *l*-menthone, by reduction of the oxime or by heating with ammonium formate, a mixture is obtained of the four possible stereoisomeric bases containing three asymmetric carbon atoms, one of which remains of fixed sign. The bases are named *l*-menthylamine ($[\alpha]_D$ −61·9°), *l*-neomenthylamine ($[\alpha]_D$ −17·4°), *l*-*iso*menthylamine

[1] *Annalen*, 1904, **331**, 359. [2] *Trans.*, 1904, **85**, 1071. [3] *Ibid.*, 65.

($[\alpha]_D + 22{\cdot}7°$), and *l-iso*neomenthylamine ($[\alpha]_D - 3{\cdot}8°$), the numbers quoted being the specific rotatory powers of the corresponding benzoyl derivatives. The separation of the components of the basic mixture was effected by crystallisation of the hydrochlorides, bromocamphorsulphonates, camphorsulphonates, and the benzoyl and formyl derivatives.

Considerable activity has prevailed during the past year in connection with the stereoisomerism of derivatives containing tervalent nitrogen and of quaternary ammonium derivatives. H. O. Jones has published[1] an exhaustive summary of our previous knowledge of the stereochemistry of nitrogen.

A. Ladenburg[2] has continued his study of the new kind of stereoisomerism of tervalent nitrogen to which he has previously referred.[3]

He resolves synthetic stilbazoline,  , into its optically active components by the aid of *d*- and *l*-tartaric acids, and obtains the *d*- and *l*-stilbazolines, having $[\alpha]_D + 12{\cdot}16°$ and $-11{\cdot}5°$ at 20°. He then heats *l*-stilbazoline at 300°, and finds that it is converted into a mixture of *d*- and *l*-stilbazolines and a new isomeride, *l-iso*-stilbazoline. The resolution of the mixture is effected by first removing the *l*-stilbazoline as its *d*-hydrogen tartrate, and converting the base recovered from the residue into its neutral *l*-tartrate, when *l-iso*-stilbazoline *l*-tartrate separates. Salts of *l-iso*stilbazoline were also isolated by another method of separation depending on the use of *d*-camphorsulphonic acid, and in each case the purified salt yielded *l-iso*stilbazoline of $[\alpha]_D - 5{\cdot}7°$. From this fact and from differences observed between the behaviour of the corresponding salts of the stilbazolines and *l-iso*stilbazoline, Ladenburg concludes that the latter is not a mixture, but a true stereoisomeride of stilbazoline.

Kipping and Salway[4] refer to the discrepancies between the theory of Hantzsch and Werner,[5] which explains the isomerism of the oximes by assuming that the three valency directions in tervalent nitrogen do not lie in one plane, and the failure of previous attempts to resolve bases in which three different groups are attached to the tervalent nitrogen atom; they again point out that the latter experiments are indecisive owing to the possibility of a change in the valency directions attending the conversion of ter- into quinque-valent nitrogen and *vice*

[1] *Brit. Assoc. Reports*, 1904.
[2] *Ber.*, 1904, **37**, 3688.
[3] *Ibid.*, 1895, **28**, 854.
[4] *Trans.*, 1904, **85**, 438.
[5] *Ber.*, 1890, **23**, 11.

versâ. They treated *d*-hydrindamine, *l*-methylhydrindamine, *l*-menthylamine, and *l*-phenethylamine with *d*-benzylmethylacetic chloride, and in each case obtained but one acetyl derivative of the primary or secondary base; if the three nitrogen valency directions do not lie in one plane, the production of stereoisomerides would be anticipated. It is therefore concluded that the three valency directions of tervalent nitrogen lie in the same plane.

It is pointed out that on treating an optically inactive base with an externally compensated acid chloride, only one acidic derivative should be formed if the original base is potentially inactive, whilst two isomerides are capable of formation if the base is externally compensated. Thus, *dl*-hydrindamine yields two isomeric acidic derivatives with *dl*-benzylmethylacetic chloride, whilst methylaniline, *p*-toluidine, benzylaniline, and phenylhydrazine yield but one product in each case. Some months later, E. Mohr described[1] the same method for ascertaining whether a base is potentially inactive or whether it is externally compensated. In studying the following reaction,

$$CH_2Ph{\cdot}CHEt{\cdot}COCl + NH_2{\cdot}CHPhMe = CH_2Ph{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}CHPhMe + HCl,$$

using externally compensated materials, he found that two isomeric compounds were formed; this is, of course, due to the potential optical activity of both the reacting substances.

Externally compensated hydrindamine may be resolved by treatment with *d*-benzylmethylacetic chloride; the least soluble of the two products of the reaction is *d*-benzylmethylaceto-*d*-hydrindamide. Similarly, *dl*-*α*-phenethylamine is resolvable by the aid of the same acid chloride, and *d*-benzylmethylaceto-*l*-phenethylimide is readily separable from the product. In these two cases, it was found impossible to regenerate the optically active bases by the hydrolysis of the acidic derivative.

The question as to the distribution in space of the three valency directions of a tervalent nitrogen atom has been also dealt with by H. O. Jones and J. P. Millington.[2] These workers were unable to resolve either phenylbenzylhydrazine, $CH_2Ph{\cdot}NPh{\cdot}NH_2$, by the aid of *d*-camphorsulphonic acid, or methylaniline-*p*-sulphonic acid by crystallisation with cinchonine.

H. O. Jones[3] prepared phenylbenzylmethylethylammonium iodide, introducing the alkyl groups in three different orders, namely, by combining benzyl, methyl, and ethyl iodides respectively with tertiary base, but obtained no evidence bearing on the occurrence of Wedekind's *α*- and *β*-isomerism. He resolved the quaternary iodide by Pope and Harvey's method,[4] applying the silver salt of *d*- and

[1] *Ber.*, 1904, **37**, 2702.
[2] *Proc. Camb. Phil. Soc.*, 1904, **12**, 489.
[3] *Trans.*, 1904, **85**, 223.
[4] *Ibid.*, 1901, **79**, 76.

l-camphorsulphonic acids in a water-free solvent. The sparingly soluble salts are *d*-B *d*-A and *l*-B *l*-A, and give $[M]_D$ + 71·0° and − 71·2° in aqueous solution. The basic ions therefore have $[M]_D$ + or − 19·5°. The optically active iodides give $[\alpha]_D$ + 8·3° and − 8·4° in alcoholic solution; they undergo autoracemisation in chloroform solution, much as do the *d*- and *l*-phenylbenzylmethylallylammonium iodides. Crystallographic measurements showed that the inactive iodide is either pseudoracemic or a mechanical mixture. The corresponding *l*-bromide gives $[\alpha]_D$ − 13·4° in alcoholic solution; its rotatory power diminishes on recrystallisation from alcohol. Thomas and Jones [1] have also resolved phenylbenzylmethyl*iso*propyl- and *iso*amyl-ammonium iodides into their enantiomorphously related components.

E. Wedekind and F. Oberheide [2] have prepared the following quaternary ammonium iodides containing asymmetric nitrogen atoms: *p*-tolylmethylethylallylammonium iodide, benzyl-*p*-tolylmethylallylammonium iodide, benzyl-*p*-tolylethylallylammonium iodide, and benzyl-*o*-tolylmethylallylammonium iodide, but have not resolved them into optically active components.

A. W. Harvey [3] has prepared phenyldimethylallylammonium iodide from dimethylaniline, but was unable to resolve the corresponding *d*-camphorsulphonate into fractions containing an optically active basic ion.

H. O. Jones [4] has obtained two stereoisomeric phenylmethylallyl-*l*-amylammonium iodides by the combination of methyl-*l*-amylaniline with allyl iodide; one of the products is dextrorotatory and the other lævorotatory. In chloroform solution, the rotatory powers of the salts gradually change until a constant value is reached owing to dissociation, which causes optical inversion of the asymmetric nitrogen atom. More recently, M. Scholtz has extended [5] Jones's study of compounds containing both an asymmetric carbon and nitrogen atom. The combination of *n*-ethylconiine with benzyl iodide leads to the formation of two isomeric benzylethylconinium iodides of different melting points and rotatory powers. Similar results were obtained on combining *n-iso*-amylconiine with benzyl iodide and *n*-benzylconiine with methyl iodide. Scholtz, however, has not observed any change of rotatory power of the isomerides such as is recorded by Jones.

On treating *dl*-dihydro-α-methylindole with *d*-bromocamphorsulphonic acid, W. J. Pope and G. Clarke [6] obtained *l*-dihydro-α-methylindole *d*-bromocamphorsulphonate ($[M]_D$ + 278° in water) as the least soluble salt; the basic ion therefore has $[M]_D$ + 5°, and on treating the salt with alkali, *l*-dihydro-α-methylindole was obtained. A second

[1] *Proc. Camb. Phil. Soc.*, 1904, **13**, 33.
[2] *Ber.*, 1904, **37**, 2712 and 3894.
[3] *Trans.*, 1904, **85**, 412.
[4] *Proc. Camb. Phil. Soc.*, 1904, **12**, 466.
[5] *Ber.*, 1904, **37**, 3627.
[6] *Trans.*, 1904, **85**, 1330.

salt of $[M]_D$ $+242{\cdot}7^\circ$ was isolated, but this does not give active base with alkali despite the low value of the molecular rotatory power; it is suggested that this salt really contains the active base, but that during the action of the alkali tautomeric change takes place in such a way that the optical activity of the base is lost.

Tattersall finds [1] that *dl*-hydrindamine is conveniently resolved by first crystallising it with *d*-tartaric acid, when *d*-hydrindamine hydrogen *d*-tartrate is obtained pure, and crystallising the base recovered from the mother liquors with *d*-bromocamphorsulphonic acid; the latter process yields *l*-hydrindamine *d*-bromocamphorsulphonate in a state of purity. On crystallising *d*- and *l*-hydrindamines with *d*-chlorocamphorsulphonic acid, indications of the production of more than one salt from each base are obtained, just as when *d*-bromocamphorsulphonic acid is used.[2]

Lastly, it should be noted that Kipping has prepared the asymmetric silicon compound, phenylethylpropylsilicon chloride, PhEtPrSiCl, but has not yet announced its resolution into components owing optical activity to the presence of an asymmetric silicon atom.[3]

W. J. Pope.

[1] *Trans.*, 1904, **85**, 169. [2] Kipping and Tattersall, *ibid.*, 1903, **83**, 918.
[3] *Proc.*, 1904, **20**, 15.

ANALYTICAL CHEMISTRY.

Although it is no exaggeration to say that chemical analysis is the foundation stone on which the greater part of the wonderful superstructure of modern chemistry has been reared, it is, and must for ever remain, in a sense, the servant of the other branches of our Science. Restricted as it is to the solution of problems involving the identification and composition of various specimens of matter, we are necessarily concerned in a report such as this with improvements and developments of technique rather than with the elaboration of new theories, or the review of great discoveries. For the sake of clearness it will be well in reviewing the advances which have been made in this branch of applied chemistry during the past year if the matter is roughly classified, and I propose therefore to deal with the subject under the following headings:

1. Inorganic analysis including electrochemical methods.
2. Organic analysis.
3. Analysis of foods and drugs.
4. Apparatus.

It will, of course, be obvious that any such sub-division must be to a certain extent arbitrary, and in some cases it has been found difficult to decide under which heading a certain process should be grouped, but it is felt that the method adopted is that which is likely to be most generally useful, and open perhaps to the fewest objections. The passing of the Food and Drugs Acts in this country and the existence of similar adulteration acts in other States have created what is virtually a special branch of analytical chemistry, having its own objects, and even its own methods, and it has therefore been thought better to deal with questions concerning the analysis of foods and drugs in a special section.

Inorganic Analysis.

In the qualitative section of this branch of analysis there is comparatively little of importance to chronicle. Numerous papers have

been published during recent years in which attention is called to the fact that a good many organic compounds may, with advantage, be pressed into the service of both qualitative and quantitative inorganic analysis. In the former case, the reactions usually consist of colour changes, and are open, very often in a marked degree, to the general objections which can so frequently be urged against such indications. Thus Matignon [1] suggests the employment of tannin and of ether containing traces of vinyl alcohol as tests for traces of vanadic acid, whilst Pozzi-Escot [2] recommends the use of the former reagent as a delicate test for molybdenum. Diphenylcarbazide, again, which has previously been recommended by Cazeneuve as a sensitive reagent for mercury, copper, ferric iron, and chromic acid, and by Lecocq for molybdenum, is now recommended by Moulen [3] as a delicate test for traces of mercuric chloride in calomel and other mercurous preparations. Lacombe [4] has suggested a new separation of cerium from yttrium earths depending on the fractional crystallisation of the double manganese nitrates from nitric acid solutions, a process which is said to give better results than that of Demarçay. Benedict [5] has proposed a simple method for the detection of nickel in the presence of a large excess of cobalt, which would appear to be useful in some cases, Autenrieth [6] indicates a useful microchemical method for the detection of strontium in the presence of calcium and barium, and Reichard [7] has studied the well-known nitroprusside reaction for sulphides and has determined its limits of sensitiveness. Donau [8] has described an interesting microchemical method for detecting traces of gold, depending on the red colour developed in silk threads previously treated with a reducing agent. Instructions are given for obtaining the solution of gold free from elements such as iron and arsenic, which would interfere, and it is stated that gold can be detected in a mineral mixture containing only one ten-millionth part by weight of that metal. The same author also finds that the colorations produced in borax beads by gold, platinum, and silver permit, under proper conditions, of the detection of exceedingly minute quantities of these metals.

In the domain of quantitative inorganic chemistry, some of the most useful papers, although those which often attract the least attention, are contributions dealing with investigations undertaken for the purpose of determining more clearly the limits of accuracy of well-known processes under the conditions obtaining in ordinary laboratory practice, and of ascertaining to what extent the results are liable to be influenced by the presence, in varying proportions, of such acids or bases as are usually found in association with the element to be deter-

[1] *Compt. rend.*, 1904, **138**, 82.
[2] *Ibid.*, 200.
[3] *L'Union Pharm.*, 1904, **45**, 147.
[4] *Bull. Soc. chim.*, 1904, **31**, 570.
[5] *J. Amer. Chem. Soc.*, 1904, **26**, 695.
[6] *Ber.*, 1904, **37**, 3882.
[7] *Zeit. anal. Chem.*, 1904, **43**, 222.
[8] *Monatsh.*, 1904, **25**, 545 and 913.

mined. Work of this character is of the highest importance, for even the most experienced analyst is apt at times to fail to realise how far some of our common reactions may fall short of the ideal limiting cases, or to what extent associated substances may interfere. Thus, Hulett and Duschalk[1] have confirmed the statement of Richards and Parker, that when barium chloride is used as the precipitant the barium sulphate obtained may contain an amount of chlorine equal to 1 per cent. of its weight. Silberberger[2] has, moreover, shown that when barium sulphate is precipitated in the presence of ferric salts, a small proportion of the iron is carried down as a double sulphate, whilst a little of the sulphuric acid remains in solution. The possible contamination of the barium sulphate with iron has, of course, been well known for a long time, but Silberberger further states that nitrates as well as potassium may contaminate the precipitate to an appreciable extent. It should be pointed out, however, that Lunge[3] denies that basic ferric sulphates are formed in the analysis of pyrites, from which the sulphuric acid cannot be washed out, and contends that the alcoholic strontium chloride method proposed by Silberberger is inaccurate when applied to the analysis of that mineral. Knight,[4] Stolberg,[5] and Hillebrand all assert that a single precipitation does not suffice to effect the complete separation of calcium from magnesium, but that a second is essential if the greatest possible accuracy is aimed at; Blount,[6] on the other hand, has shown that under proper conditions one operation, in the case of cement analysis, at least, is capable of yielding results in which any error is so slight as to be quite negligible. Persulphates are now finding somewhat extensive employment as oxidising agents in analytical operations, and during the past year one or two new uses for these salts have been suggested. Thus, Imbert and Dumolard[7] have shown that the ammonium salt furnishes a convenient means of estimating bromide in the presence of chloride, the former being decomposed into bromine and bromate, whilst the latter remains unattacked. G. v. Knorre,[8] again, has shown that whilst it is impossible to effect a sharp separation of manganese from copper, zinc, cadmium, nickel, and magnesium by means of ammonium persulphate, that substance permits of a very accurate separation of manganese and chromium, the former being precipitated as the peroxide and the latter converted into chromic acid. This method has been applied with good results to the estimation of manganese in iron by Lüdert.[9]

[1] *Zeit. anorg. Chem.*, 1904, **38**, 196.
[2] *Monatsh.*, 1904, **25**, 220.
[3] *Zeit. angew. Chem.*, 1904, **17**, 949.
[4] *Chem. News*, 1904, **89**, 146.
[5] *Zeit. angew. Chem.*, 1904, **17**, 741 and 769.
[6] *J. Soc. Chem. Ind.*, 1904, **23**, 1218.
[7] *Ann. Chim. anal.*, 1904, **9**, 21.
[8] *Zeit. anal. Chem.*, 1904, **43**, 1.
[9] *Zeit. angew. Chem.*, 1904, **17**, 422.

In connection with the above work of v. Knorre, Dittrich and Hassel[1] have more recently shown that the separation of manganese from the above-mentioned metals can be completely effected if a second precipitation is resorted to, and that even a single operation suffices when they are present in comparatively small quantities. Friend[2] has called attention to the fact that hydrogen peroxide can only be accurately estimated by permanganate in the presence of persulphates under certain well-defined conditions, which are not those ordinarily observed. As instances of useful revision work, attention may be called to the extensive investigation by Daniel[3] of the Wöhler-Fresenius method for the estimation of fluorine, and to the paper by Waring[4] on the volumetric ferrocyanide method of estimating zinc. In the first case, the author confirms the accuracy of the process, and indicates fully the precautions which have to be taken in order to obtain the best results, whilst in the second attention is directed to several important sources of error. Gutbier, Metzner, and Lohmann[5] have made a comparative study of the various gravimetric methods for the estimation of selenium, and have found the majority more or less unsatisfactory, although good results can be obtained by employing hydrazine salts as the reducing agents. For the estimation of uranium in uranyl compounds, Glasmann[6] has proposed an iodometric method which gives good results and appears susceptible of useful application. Lunge[7] has very carefully compared the permanganate and sulphanilic acid methods for estimating nitrite, and has come to the conclusion that whilst there is very little difference between them in point of accuracy, the far greater simplicity and convenience of the permanganate process marks it out for general adoption. The same author has published a series of papers[8] dealing with *Indicators, iodometry, and the selection of standard substances for alkalimetric titrations*, in which a number of points of interest and importance to analysts are dealt with. In connection with iodometry, it may be mentioned that Young[9] states that he has used anhydrous sodium thiosulphate for the standardisation of iodine solutions with excellent results. Raschig[10] prepares for the same purpose a standard solution of sulphur dioxide by passing the gas into water, weighing, and then diluting to a known volume. He also recommends a similar method for preparing standard solutions of hydrogen chloride, but the principle is not by any means new, having been suggested some years ago by Moody.[11]

[1] *Zeit. anal. Chem.*, 1904, **43**, 382.
[2] *Trans.*, 1904, **85**, 597.
[3] *Zeit. anorg. Chem.*, 1904, **38**, 257.
[4] *J. Amer. Chem. Soc.*, 1904, **26**, 4.
[5] *Zeit. anorg. Chem.*, 1904, **38**, 291.
[6] *Ber.*, 1904, **37**, 189.
[7] *Chem. Zeit.*, 1904, **28**, 501.
[8] *Zeit. angew. Chem.*, 1904, **17**, 195, 225, and 265.
[9] *J. Amer. Chem. Soc.*, 1904, **26**, 1028.
[10] *Zeit. angew. Chem.*, 1904, **17**, 577.
[11] *Trans.*, 1898, **78**, 658.

Titanium in the tervalent condition, which has already been recommended by Knecht as a reducing agent in organic analysis, is found by Stähler [1] to constitute a convenient reagent for the volumetric estimation of hydroxylamine. The results are accurate, and the method would appear to be capable of extended employment. Attention may here be directed to an interesting paper by McCoy [2] dealing with the ionisation constants of phenolphthalein in relation to the employment of that substance as an indicator, and also to one by Green and Perkin [3] on another aspect of the same subject.

During recent years, many organic substances have been suggested for use in quantitative estimations and separations, some of which appear to be capable of useful employment. One of the first, and one which is susceptible of somewhat wide application, is nitroso-β-naphthol; this substance has now been found by G. v. Knorre [4] to be capable of effecting the complete separation of iron from zirconium. Neish [5] finds that thorium can be quantitatively separated in two precipitations from cerium, lanthanum, and didymium by *m*-nitrobenzoic acid, and that the process gives good results in the analysis, for example, of monazite sands. In this connection, it is interesting to note that Erdmann and Makowka [6] have found that palladium can be readily separated by means of acetylene from platinum, iridium, rhodium, gold, and copper. Hydrazine is another reagent which has of late found somewhat extensive application in analytical operations, and Jannasch and Bettges [7] have recently shown that by its aid mercury can be separated from molybdenum and tungsten, and that palladium [8] and platinum in the presence of ammonia [9] may be separated from many other metals and estimated. Schlötter [10] has also found that iodates and chlorates are, like bromates, reduced by hydrazine sulphate to the corresponding halides. Plimmer [11] has shown that silver cyanide may be separated from the chloride by boiling with dilute nitric acid, and that the drastic treatment originally recommended for this purpose by Kraut is not necessary. An apparently useful process for the estimation of iodide, bromide, and chloride, when present together, has been devised by Thilo,[12] depending on the order in which the silver halides are formed on the addition of silver nitrate. A number of processes capable of giving fair results and involving the use of hydrazine salts have, during recent years, been

[1] *Ber.*, 1904, **37**, 4732.
[2] *Amer. Chem. J.*, 1904, **31**, 503.
[3] *Trans.*, 1904, **85**, 398.
[4] *Zeit. angew. Chem.*, 1904, **17**, 641 and 676.
[5] *J. Amer. Chem. Soc.*, 1904, **26**, 780.
[6] *Ber.*, 1904, **37**, 2694.
[7] *Ibid.*, 2210, 2219
[8] Jannasch and Rostosky, *Ber.*, 1904, **37**, 2441.
[9] Jannasch and Stephan, *ibid.*, 1980.
[10] *Zeit. anorg. Chem.*, 1904, **38**, 184.
[11] *Trans.*, 1904, **85**, 12.
[12] *Chem. Zeit.*, 1904, **28**, 866.

suggested for the gasometric estimation of certain metals, and Girard and Saporta [1] have recently further investigated the method as applied to the estimation of copper and nitrites. The author of this report [2] has directed attention to the use of palladium-hydrogen as a reducing agent in quantitative analysis, and has pointed out that this substance may be used with great advantage in the conversion of ferric into ferrous salts, chromates into chromic salts, ferricyanides into ferrocyanides, and ceric into cerous salts, inasmuch as complete reduction is in all these cases readily effected, and the resulting solution is of course not contaminated with any products derived from the reducing agent. He has also found that "uncharged" palladium dissolves readily in acid solutions of ferric and cupric chlorides, palladious chloride being formed together with the lower chlorides of each of the above metals. In a number of other cases which have been studied, reduction either does not occur at all or is very incomplete. Morgan [3] has recorded some experiments on the separation and estimation of arsenic by distillation in hydrogen chloride and hydrogen sulphide, a method which was some years ago proposed by Piloty and Stock for the separation of arsenic and antimony. This paper, which deals with the separation of arsenic in its two states of oxidation, may be usefully consulted by all who have to estimate that element in minerals and other natural products.

The direct estimation of boron in minerals was for long so difficult a matter, and the results obtained were so uncertain, that this element was usually determined by difference. Schaak [4] has now applied the well-known methods of Thomson and of Gooch to naturally-occurring borates, and finds that good results can be obtained.

In electrochemistry, as applied to analytical separations and estimations, much progress has been made during the year, the work of Hollard and his colleagues being of special importance. The impossibility of effecting the separation of metals the electrolytic potentials of which are higher than that of hydrogen is well known, the difficulty being, of course, due to the liberation of hydrogen at the cathode, and to the virtually increased resistance of the cell. Freudenberg was one of the first to recognise and study the bearing of variations of tension in electrolytic separations, and much work on this subject has since been done. Hollard has now shown that the difficulties above referred to in connection with the high polarisation potentials of certain metals may be largely overcome by constructing the anode of a soluble metal or by surrounding it with a reducing solution, and in this way it has been found practicable to separate, for example, zinc from nickel. In addition to this, he has made many

[1] *Bull. Soc. chim.*, 1904, **31**, 905.
[2] *Analyst*, 1904, **29**, 346.
[3] *Trans.*, 1904, **85**, 1001.
[4] *J. Soc. Chem. Ind.*, 1904, **23**, 699.

experiments in the direction of constructing the cathode of other metals than platinum with very useful results. The principle of separation by the use of complex salts is dealt with in a paper by Hollard and Bertiaux,[1] who show that nickel may be separated from zinc and zinc from iron by converting the zinc into zinc-ammonium nitrite and the iron into potassium ferrocyanide. This method is, however, to some extent limited in its application by the fact that certain complex ions (for example, the double cyanides of gold, silver, cadmium, and mercury with potassium) themselves appear to dissociate, and so permit the deposition of the heavy metal on the cathode. In extension of the recently published work of Edgar F. Smith,[2] Meyers[3] has made further experiments with mercury cathodes, and has found that chromium can be accurately estimated in sulphuric acid solutions, and has been successful in effecting a number of important separations. Other papers have been published by Perkin and Prebble, Richards, Gallo, Amberg and others dealing with improved forms of electrodes or cells, and with the improvement of existing processes. The adoption of a rotating anode together with the employment of comparatively high pressure currents have enabled Ingham[4] to effect successfully the estimation of zinc, and in the hands of Ashbrook[5] similar conditions have given good results in the quantitative separation of a number of metals which have not hitherto proved amenable to electrolytic treatment. Hollard and Bertiaux[6] discuss the electrolytic separation of bismuth and copper, and describe a useful method for estimating very small quantities of the former metal in the presence of large amounts of lead. As another example of the application of the methods above referred to, attention may be called to the electrolytic separation by Coehn and Kettembeil[7] of the alkali-earth metals. A recent paper by Hollard[8] may be usefully consulted by all who employ the electrolytic method for the estimation of lead. In this it is shown that the composition of the "peroxide" deposited on the anode, and consequently the analytical factor to be used, depends not only on the concentration of the electrolyte, but also on the physical character of the electrode. A paper by the same author and Bertiaux[9] dealing with the assay of alloys of platinum, gold, and silver is virtually a criticism of the methods of assaying in vogue in France, and may be usefully referred to by all interested in this branch of analysis.

The attention of water analysts is directed to an interesting series

[1] *Bull. Soc. chim.*, 1904, **31**, 900.
[2] *J. Amer. Chem. Soc.*, 1903, 25, 883.
[3] *Ibid.*, 1904, **26**, 1124.
[4] *Ibid.*, 1269.
[5] *Ibid.*, 1283.
[6] *Bull. Soc. chim.*, 1904, **31**, 1131.
[7] *Zeit. anorg. Chem.*, 1904, **38**, 198.
[8] *Compt. rend.*, 1904, 138, 142.
[9] *Ann. Chim. anal.*, 1904, **9**, 287.

of analyses of waters from the oolite-formations by Fisher,[1] which go to show that whenever these are covered by clay, alkaline supplies are obtained, whilst hard calcareous water is invariably got from the uncovered beds.

Two papers dealing with the solubility of salts have appeared during the year, the one by Kohlrausch,[2] who has calculated from the electric conductivity of saturated solutions the solubility in water of a number of sparingly soluble salts, the other by Naumann,[3] who gives the solubility of a very large number of metallic derivatives in acetone and pyridine solutions.

Comparatively little advance has been made in connection with the analysis of gases, but Wohl[4] calls attention to the very appreciable error which may sometimes be introduced into the results of gas analysis, made by combustion methods, by assuming that the molecular volumes of all gases are the same, and urges that the true molecular volumes according to the latest determinations should in all cases be taken. Richardt[5] has studied the fractional combustion of gases containing hydrogen when mixed with air and passed over heated palladium wire, and Pfeiffer[6] has proposed an improved method for the estimation of benzene in coal gas, in which the dinitrobenzene obtained is estimated volumetrically.

All who are interested in technical calorimetry, with more especial reference to the examination of coal, will read with considerable interest a paper by Gray and Robertson,[7] in which several different types of calorimeter are compared and their indications discussed.

Organic Analysis.

For the rapid and simultaneous detection of the halogens, phosphorus, arsenic, and sulphur in organic compounds, Pringsheim[8] has recommended a useful and simple method in which sodium peroxide is employed as the oxidising agent.

Kling and Viard[9] have shown that the different behaviour of primary, secondary, and tertiary fatty alcohols, when heated, affords a method of differentiating between them, which may in some cases be usefully employed either in place of, or in addition to, the existing well-known methods. A number of reactions have been described by various authors for the detection and identification of certain organic compounds, but these, whilst in many cases useful, are scarcely of

[1] *Analyst*, 1904, **29**, 29.
[2] *Zeit. physikal. Chem.*, 1904, **50**, 355.
[3] *Ber.*, 1904, **37**, 4328 and 4609.
[4] *Ibid.*, 429.
[5] *Journ. Gasbeleucht*, 1904, **47**, 566 and 590.
[6] *Chem. Zeit.*, 1904, **28**, 884.
[7] *J. Soc. Chem. Ind.*, 1904, **23**, 704.
[8] *Ber.*, 1904, **37**, 2155.
[9] *Bull. Soc. chim.* 1904, **31**, 783.

sufficient general interest or importance to merit special reference. An exception may perhaps be made in favour of the method proposed by Freundler [1] for the identification and approximate estimation of methyl anthranilate, since this should be capable of somewhat wide application.

Collie [2] has described a method for the estimation of carbon and hydrogen in certain organic compounds, based upon that first suggested by Saussure and Prout, in which the weighed substance is burned in a measured volume of oxygen. It is pointed out that in the case of those compounds to which it can be applied the method has the merits of accuracy and rapidity of execution, whilst the very small amount of substance required constitutes a still further advantage. Morgan [3] recommends the use of phosphoric acid, on account of its non-volatility, for the decomposition of carbonates in the direct estimation of carbon dioxide, and states that organic carbon, when present, may be determined in the residue by the chromic acid method with good results. Combustion with sodium peroxide has been employed by Pringsheim [4] for the estimation of halogens, phosphorus, and arsenic in organic compounds with excellent results, and von Konek [5] has also recommended the use of this oxidising agent, although under somewhat different experimental conditions. The last-named author points out that whilst a similar process may be employed in some cases for the estimation of nitrogen, a number of compounds, for example, pyridine and quinoline, do not yield the whole of their nitrogen as nitrate. In many instances, it is clear that peroxide "combustion" may be advantageously employed in ultimate organic analysis, but, on the other hand, a perusal of some of the published papers produces the impression that the method has been recommended for estimations which can be far more easily and accurately carried out by the ordinary well-known methods. Attention may also be called to the chromic acid oxidation process for the estimation of halogens in organic compounds proposed by Baubigny and Chavanne,[6] which is stated to give very accurate results.

Kjeldahl's method for estimating nitrogen continues, as is natural, to attract the attention of investigators, and modifications (many of which do not constitute improvements) are from time to time suggested. R. B. Gibson [7] has shown that, contrary to the statement of Kutscher and Steudel, the nitrogen in creatine, uric acid, hippuric acid, and some similar compounds can be accurately estimated by this process,

[1] *Bull. Soc. chim.*, 1904, **31**, 882.
[2] *Trans.*, 1904, **85**, 1111.
[3] *Ibid.*, 1004.
[4] *Amer. Chem. J.*, 1904, **31**, 386.
[5] *Zeit. angew. Chem.*, 1904, **17**, 886, 888, and 1093.
[6] *Bull. Soc. chim.*, 1904, **31**, 396.
[7] *J. Amer. Chem. Soc.*, 1904, **26**, 105.

whilst Sherman and Falk[1] are of opinion that the Gunning-Kjeldahl method, when carried out as suggested by Dyer,[2] combines all the advantages of the other modifications of this method. In this paper, attention is called to the fact that it is in many cases necessary to continue the sulphuric acid digestion for some time after the liquid has become colourless. It is well known that the use of glass for the purpose of condensing the ammoniacal steam may introduce an appreciable error into the determination, and Schönewald and Bartelt[3] have examined the behaviour of different kinds of glass in this respect.

Debordeaux[4] has devised a method based on distillation with potassium thiosulphate and potassium sulphide for the determination of nitrogen, which is applicable to a large number of organic compounds differing widely in character, and which is said to yield pure ammonia without any admixture of amines such as sometimes occurs with other processes.

Hibbert and Sudborough[5] have investigated the magnesium alkyl haloid method proposed by Tschugaeff for the detection of hydroxyl groups, and have found that with proper precautions good quantitative results can be obtained. A. G. Perkin[6] has described a method for the determination of acetyl groups, which is simple and yields good results.

Stritar and Zeidler[7] recommend for the determination of methyl alcohol a slight modification of the method devised by Zeisel and Fanto for the estimation of glycerol. In this, the alcohol is converted into methyl iodide and weighed as silver iodide. The process is recommended for the estimation of methyl alcohol in commercial formaldehyde, in wood spirit, and in crude pyroligneous acid. While referring to the above-mentioned method for glycerol estimation, it may be pointed out that, following on the adverse criticism of Lewkowitsch, Fanto[8] has been led to modify the original conditions, having found, after further investigation, that correct results cannot be obtained in the estimation of glycerol in fats by treating the fat directly with the hydriodic acid. In connection with the analysis and evaluation of essential oils, much work has been done, an ever-increasing body of investigators being attracted to this comparatively new field of research. The majority of the published papers deal either with the investigation of new products or with the detection of adulterants in the more expensive oils of commerce, and, even if they were of sufficient general interest, are so numerous that it is impossible to refer to more than a

[1] *J. Amer. Chem. Soc.*, 1904, **26**, 1469.
[2] *Trans.*, 1895, **67**, 811.
[3] *Woch. Brau.*, 1904, **21**, 793.
[4] *Compt. rend.*, 1904, **138**, 905.
[5] *Trans.*, 1904, **85**, 933.
[6] *Proc.*, 1904, **20**, 171.
[7] *Zeit. anal. Chem.*, 1904, **43**, 387, 401.
[8] *Zeit. angew. Chem.*, 1904, **17**, 420.

few of them in this report. Burgess[1] has shown that the method previously suggested by him for the estimation of citral in oil of lemon is applicable to the estimation of aldehydes and ketones in a number of other essential oils. This method, which depends on the fact observed by Tiemann that when a neutral sulphite in solution is added to an aromatic or fatty aldehyde an additive compound is formed with the simultaneous production of sodium hydroxide, which can, of course, be titrated, has also been investigated by Sadtler,[2] who arrives at the same conclusion as Burgess. The method of estimating cinnamaldehyde as semi-oxamazone recently proposed by Hanus has been examined in Schimmel's laboratory, and is stated to be of considerable utility.[3] The method proposed by Bamber for the examination of citronella oil [4] has now been adopted as official by the Ceylon Government, but has been adversely criticised by Schimmel.[5] Rose oil has been usefully studied from the analytical point of view by Jeancard and Satie,[6] and also by Hudson-Cox and W. H. Simmons.[7] The last-named author [8] has continued his work on the iodine absorption of attar of rose, and has obtained results which confirm his opinion as to the value of this test in judging the purity of this oil, but the refractive index is found to be of very little value for this purpose. The sodamide method suggested by Schryver for the determination of phenols in essential oils has been further examined in Schimmel's laboratory, and has been found inapplicable in the presence of alcohols. As Schryver has already shown that aldehyde and ketones also interfere, it is clear that its employment must be restricted to oils consisting solely of hydrocarbons and phenols, in which cases it gives very satisfactory results. The increasing and more refined adulteration of turpentine has led many chemists during the past few years to devise and study new methods for its detection, and papers by Worstall,[9] Harvey,[10] and McCandless [11] are useful contributions to this subject. Some attention has been devoted during the past year to the study of the colour reactions of certain fixed oils with the object of ascertaining to what extent they might be relied on as evidence of sophistication, and, speaking generally, it may be said that the results have shown them to be less trustworthy than is often assumed. Some of these will be referred to in the section dealing with the analysis of foods and drugs. Several investigators have devoted attention to the comparison and extended study of the better known iodine absorption processes, among the more

[1] *Analyst*, 1904, **29**, 78.
[2] *J. Soc. Chem. Ind.*, 1904, **23**, 303.
[3] *Schimmel's Report*, 1904, April/May.
[4] *Proc.*, 1903, **19**, 292.
[5] *Report*, 1904, October/November.
[6] *Bull. Soc. Chim.*, 1904, **31**, 934.
[7] *Analyst*, 1904, **29**, 175.
[8] *Chemist and Druggist*, 1904, **65**, 703.
[9] *J. Soc. Chem. Ind.*, 1904, **23**, 302.
[10] *Ibid.*, 413.
[11] *J. Amer. Chem. Soc.*, 1904, **26**, 981.

important papers being one by Archbutt,[1] who has compared the iodine-bromide method with that of Wijs in favour of the latter, and one by Tolman,[2] in which the methods of Hübl, Wijs, Hanus, and McIlhiney are reported on. From the more purely scientific point of view, a paper by Ingle [3] on the iodine value of unsaturated organic compounds will be found to be of considerable interest. The method recently proposed by Partheil and Ferié for the separation and estimation of saturated fatty acids, and which was based upon differences in the solubilities of their lithium salts, has been examined by Fahrion [4] and by Farnsteiner,[5] both of whom report it to be untrustworthy. Lewkowitsch [6] has proposed the hexabromide test as a means of differentiating between linseed and "boiled" oils, and has described the analytical reactions of some almond and allied oils. The detection of the adulteration of beeswax has been usefully dealt with by Cohn.[7] In connection with the chemistry of the sugars, Ofner [8] has studied the phenylmethyl- and phenylbenzyl-hydrazine derivatives of the aldoses, and is of opinion that these compounds may be usefully employed in analytical operations, whilst Neuberg [9] confirms his previous statement that phenylmethylhydrazine is capable of being successfully used for the detection of lævulose in the presence of dextrose, and for its identification in carbohydrate mixtures.

Descriptions of new processes for the estimation of the sugars, many of which are characterised by considerable ingenuity, are constantly being published, but, apart from some special application, they do not constitute any improvement on the gravimetric Fehling method, which is now, in one form or another, almost universally adopted. Thus Rosenthaler [10] proposes to titrate the acids formed by the oxidation of the reducing sugars by Fehling's solution, whilst Oerum [11] suggests the solution and colorimetric estimation of the reduced cuprous oxide.

In an interesting paper,[12] Noyes, Crawford, Jumper, Flory, and Arnold describe experiments made on the rate and extent of the hydrolysis of maltose and dextrin as effected by dilute acids, and give a method for the estimation of starch which properly includes a preliminary hydrolysis of that substance by diastase. It is strange that, in spite of all the work done during recent years, so many authors should still recommend direct acid inversion methods for starch estimation, and burden chemical literature with the more or less inaccurate results obtained. That the optical rotations of certain of the sugars

[1] *J. Soc. Chem. Ind.*, 1904, **23**, 306.
[2] *J. Amer. Chem. Soc.*, 1904, **26**, 826.
[3] *J. Soc. Chem. Ind.*, 1904, **23**, 422.
[4] *Zeit. angew. Chem.*, 1904, **17**, 1482.
[5] *Zeit. Nahr. Genussm.*, 1904, **8**, 129.
[6] *Analyst*, 1904, **29**, 2.
[7] *Zeit. öffentl. Chem.*, 1904, **10**, 404 and 415.
[8] *Ber.*, 1904, **37**, 3362 and 4399.
[9] *Ibid.*, 4616.
[10] *Zeit. anal. Chem.*, 1904, **43**, 282.
[11] *Ibid.*, 356.
[12] *J. Amer. Chem. Soc.*, 1904, **26**, 266.

are not the same in acid as in neutral solution, and cannot therefore be regarded as constant numbers, is sometimes overlooked by sugar chemists, and Remy [1] usefully calls attention to the error which may be introduced into the estimation of cane sugar by Clerget's method when lævulose is present in the original substance by the failure to recognise this fact. Ling and Rendle [2] have pointed out that concentrated malt extract invariably contains large proportions of dextrose formed naturally from the starch during manufacture, which is of importance, inasmuch as these extracts now find considerable employment in commerce, and the presence of dextrose might otherwise have been thought to indicate adulteration with glucose. Reference may here be made to a paper by Ford [3] in which he describes the precise conditions which must be observed in the determination of the pre-existent sugars in grain by extraction with alcohol. No analyst who is accustomed to make determinations of the diastatic activity of malt will need to be reminded that this arbitrary number is largely influenced by the precise temperature and time conditions adopted during extraction and digestion, but it is not as clearly recognised that other, and apparently trivial, details may affect the result to an appreciable extent, and an exhaustive paper by Ford [4] dealing with the subject will well repay careful study.

The number of new colour reactions to be obtained with various alkaloids seems to be limited only by the number of observers and by the patience and ingenuity they exhibit, and whilst some of these may be serviceable, many are obviously of very little value in ordinary analytical practice. Reichard [5] points out that cocaine yields a sparingly soluble nitroprusside which may at times be useful in effecting its separation from morphine, and gives some new colour reactions of the former alkaloid. New colour reactions of morphine are also given by Ballandier [6] and by Rosenthaler and Türk,[7] of pilocarpine by Barral,[8] and of strychnine and brucine by Reichard.[9] Léger [10] has examined the well-known André (Thalleioquin) reaction for quinine with the object of ascertaining the conditions of greatest sensitiveness. Schidrowitz [11] has compared several processes for the estimation of morphine in opium, and has described a method which is, in his opinion, superior to others both in simplicity and accuracy, and which is based to some extent on the Pharmacopœia Germanica IV process. For the estimation of codeine in the same drug, Caspari [12] describes a process

[1] *Bull. Assoc. Chim. Sucr. Dist.*, 1904, **21**, 1002.
[2] *Analyst*, 1904, **29**, 243.
[3] *Ibid.*, 277.
[4] *J. Soc. Chem. Ind.*, 1904, **23**, 414.
[5] *Chem. Zeit.*, 1904, **28**, 299.
[6] *J. Pharm. Chim.*, 1904, **19**, 151.
[7] *Apoth. Zeit.*, 1904, **19**, 186.
[8] *J. Pharm. Chim.*, 1904, **19**, 188.
[9] *Chem. Zeit.*, 1904, **28**, 977.
[10] *J. Pharm. Chim.*, 1904, **19**, 281 and **434**.
[11] *Analyst*, 1904, **29**, 144.
[12] *Pharm. Rev.*, 1904, **22**, 348.

which is stated to give good results and to be superior to that of Van der Wielen. Staněk [1] points out that betaine can, under certain conditions, be quantitatively precipitated by a solution of iodine in potassium iodide, and may thus be separated from glycine, asparagine, tyrosine, and other substances with which it is often associated. This method when fully worked out would appear to be capable of useful application.

Barger and Shaw [2] have shown that Keller's process for the assay of digitalis tinctures gives results far below the truth, and they are of opinion that at present the physiological method is the only reliable one. Several papers dealing with the estimation of tannin and the analysis of tanning materials have been published during the year. Perhaps the most important of these is one by Parker and Payne [3] describing a process which is said to be in many respects superior to the well-known hide-powder process. This method has, however, been criticised by Dreaper,[4] who recommends for the estimation of tannic and gallic acids a modification of a process which he first described some years ago, and has also been referred to by Wood and Trotman,[5] who have made an examination of the so-called "collin" which Parker and Payne use for the precipitation of tannin. The hide-powder process in the form recommended by the Association of American Official Agricultural Chemists is dealt with by Mardick,[6] who proposes certain modifications of procedure. H. Wislicenus [7] also devotes attention to this subject, and recommends the use of a highly porous aluminous material in place of hide-powder, which is said to give results at least equally good, and to constitute a far more convenient reagent.

Analysis of Food and Drugs.

Owing to its great importance, and to the fact that it was not in the hands of the public until the beginning of 1904, the Report of the Royal Commission on Arsenical Poisoning in Food may be fittingly referred to here, notwithstanding that it was signed in November 1903. Of chief importance from the point of view of analytical chemistry is the recognition by the Commissioners of the fact that satisfactory estimations of arsenic in food-stuffs and other materials can be made by the comparison of mirrors obtained by the employment of the Marsh-Berzelius method. This process, which had previously been suggested for the purpose by the Joint Committee appointed by the Societies of Chemical Industry and Public Analysts, has now been

[1] *Zeit. Zuckerind. Böhm.*, 1904, **28**, 578.
[2] *Pharm. J.*, 1904, **18**, 249.
[3] *J. Soc. Chem. Ind.*, 1904, **23**, 648.
[4] *Chem. News*, 1904, **90**, 111.
[5] *J. Soc. Chem. Ind.*, 1904, **23**, 1071.
[6] *Ibid.*, 1187.
[7] *Zeit. angew. Chem.*, 1904, **17**, 801.

most rigorously tested, and in one form or another is almost universally employed in this country. The Commissioners remark that they do not attempt to pronounce for or against any particular modification of the Marsh-Berzelius method, and that they are satisfied that careful analysts will be able to obtain results sufficiently exact and comparable for practical purposes, even although the details of their procedure may differ. At the same time, they refer to the electrolytic process recommended by the Board of Inland Revenue Committee,[1] and indicate some of the advantages which it appears to possess over the zinc method. Owing to the wise decision of the Commission not to recommend any special form of apparatus or procedure as official or standard, and to the great difficulty of obtaining zinc of a sufficiently high degree of purity and sensitiveness, much attention has been devoted to the improvement of the electrolytic process. The Inland Revenue Committee method, above referred to, whilst excellent in many respects, suffers from the disadvantage of being less sensitive than the zinc process, and of necessitating the previous reduction of arsenates. The latter difficulty appears to have been first avoided by Trotman by the addition of zinc sulphate to the contents of the cathode compartment, and since then several investigators have experimented with cathodes constructed of other metals than platinum. Thus, Sand and Hackford [2] recommend lead for this purpose and describe a form of apparatus which is said to be highly sensitive, inasmuch as it will detect 0·0000005 gram of arsenic in 50 c.c. of liquid, and also very convenient. Arsenates are readily reduced, and it is stated that commercial lead "absolutely free from arsenic and antimony" can be obtained. It is to be noted, however, that W. Thomson,[3] who has also tried lead cathodes, speaks of the arsenic which it contains as coming off "gradually for a long time," and describes the results obtained as "irregular." He also recommends a special form of apparatus with a pure zinc cathode, and claims that the indications are much more sensitive than those given by the Committee's method. A report dealing with the detection of arsenic in the drugs of the British Pharmacopœia has been presented to the Pharmacopœia Committee of the General Medical Council by Dunstan and Robinson. The authors recommend a modification of the test first proposed by Mayençon and Bergeret on the ground that it is capable of easy application and avoids the working difficulties involved in the use of the Marsh-Berzelius method. In all other respects, however, the suggested test is decidedly inferior. In this connection it may be noted that Cloud [4] has employed the Marsh-Berzelius method for the estimation of

[1] *Trans.*, 1903, **83**, 974. [2] *Ibid.*, 1904, **85**, 1018.
[3] *Mem. Proc. Manchester Phil. Soc.*, 1904, **48**, 1.
[4] *J. Soc. Chem. Ind.*, 1904, **23**, 524.

minute quantities of arsenic in copper ores and metallurgical products. Another important Official Report (Final) recently issued is that of the Departmental Committee on Butter Regulations. In this there is little or no direct reference to analytical procedure, but the majority of the members recommend the adoption of twenty-four as the limiting Reichert-Wollny number, below which a presumption should be raised that butter is not genuine. The recent extensive use of cocoa-nut oil in the manufacture of margarine and in the adulteration of butter has done much to diminish the value of the indications of the Reichert-Meissl and Reichert-Wollny methods. The process, for instance, which was made official in 1900 for the estimation of butter-fat in margarine, and which was devised by the principal chemist of the Government Laboratory in collaboration with a Committee of the Society of Public Analysts, is no longer to be implicitly relied on, and will doubtless have to be modified. Polenske [1] describes a method for the determination of cocoa-nut oil in butter. This involves an estimation of the volatile insoluble in addition to the volatile soluble fatty acids distilling over in the ordinary Reichert-Meissl process ("new butter number"), and is based on the well-known fact that the proportion of the soluble to the insoluble volatile fatty acids is far higher in butter than in cocoa-nut oil. Muntz and Coudon [2] have worked out a method very similar to that of Polenske and have independently arrived at practically the same conclusion. The correctness of the principles underlying these methods does not admit of doubt, and they cannot fail to be of very great assistance in the solution of a difficult and important problem. Juckenack and Pasternack [3] also deal with this subject, and point out that whilst the ordinary constants obtained in butter analysis do not suffice to show the presence of cocoa-nut oil, a consideration of the relation existing between certain of these, coupled with a knowledge of the molecular weights of the soluble and insoluble fatty acids, suffices, in many cases, to lead to a definite conclusion. Siegfeld [4] has made further experiments with the phytosterol acetate test, and states that he has confirmed the accuracy of his previous statements that 10 per cent. of cocoa-nut or other vegetable oil can be detected in butter by its aid. Hoton [5] describes an apparently useful method for the analysis of butter based on the fractional separation of the glycerides from an acetic acid solution by cooling, and the determination of the refractive indices and Valenta numbers of the separated fractions. In connection with this subject, an important paper on "The Interdependence of

[1] *Zeit. Nahr. Genussm.*, 1904, **7**, 273.
[2] *Annales de l'Institut national agronomique*, 2° série, Tome III, Fascicule Ier.
[3] *Zeit. Nahr. Genussm.*, 1904, **7**, 193. [4] *Ibid.*, 577.
[5] *Bull. Soc. Chim. Belg.*, 1904, **18**, 147.

the Physical and Chemical Criteria in the Analysis of Butter-fat" has been published by T. E. Thorpe,[1] and will be studied by all who are interested in this branch of analytical chemistry. Several investigations have been undertaken in connection with the estimation of fat in milk, and one or two new modifications of well-known methods have been proposed, but they are scarcely of sufficient interest or importance to merit special reference. Richmond[2] gives the average composition of more than 15,000 samples of milk analysed during 1903, the average fat percentage having been 3·83 per cent. Sjollema and Visser independently[3] describe experiments made for the purpose of deciding which is the most accurate process for the estimation of fat in cheese, and arrive at the conclusion that the methods of Bondzynski and Gerber are the best, and that ether extraction gives low results. Harrison,[4] in a paper on the analysis of condensed milk, gives the results of a number of experiments made for the purpose of ascertaining the best conditions for the estimation of cane sugar and lactose, and Richardson and Jaffé,[5] dealing with the same subject, propose a polarimetric method involving readings at 20° and at 86°, the invert sugar producing, as is well known, no rotation at the higher temperature. The present high price of cod-liver oil and the consequent temptation to adulterate with vegetable or cheaper fish oils has caused the question of its analytical examination to assume considerable importance. Liverseege[6] publishes the results of an investigation of a number of genuine samples as well as of several allied liver and fish oils. From these, as well as from the results of other workers, it would appear that the detection of sophistication is often a matter of very great difficulty, but that the refractive index as determined by the butyro-refractometer of Zeiss and the Valenta test are among the most useful. The sulphuric and nitric acid colour reaction is also very good, and it is pointed out incidentally that the tests specified in the British Pharmacopœia are of very little value for the purpose of discriminating between the genuine and the adulterated oil.

During recent years, much attention has been devoted to the study of the nucleins and the derived purine bases in their relation not only to normal metabolic changes in the animal organism, but also to certain pathological conditions. Much excellent work has been done, and the increasing importance of the subject to the food chemist is becoming clearly recognised. Methods for the recognition and approximate separation of the purine bases have been known for some time, and have been applied by different observers to the examination of various foods.

[1] *Trans.*, 1904, **85**, 248.
[2] *Analyst*, 1904, **29**, 180.
[3] *Hoorn. Chemisch. Week. Vlad.*, 1904, 29.
[4] *Analyst*, 1904, **29**, 248.
[5] *J. Soc. Chem. Ind.*, 1904, **23**, 309.
[6] *Analyst*, 1904, **29**, 210.

During the past year, Micko [1] has published the results of the continuation of his detailed analytical examination of samples of meat and yeast extract, and has described the methods he has adopted for the identification of the so-called xanthine bases present. It is interesting to note that the same bases are, as might perhaps have been anticipated, present in the extract obtained from both sources, that is, meat and yeast, but in different proportions. In this connection, the results of the analysis of a number of commercial extracts of both kinds by Graff [2] will be studied with interest, as they probably represent the most accurate existing analysis of these products. Food chemists will also read with considerable interest a paper by Grindley [3] which contains a very considerable number of analyses made with the object of elucidating the chemistry of the proteids and other nitrogenous constituents existing in meats.

In connection with the detection and estimation of preservatives in food-stuffs, two recent communications are of importance, inasmuch as they show the need for the exercise of caution in drawing conclusions from the presence of very small quantities of certain substances which happen to be widely used as preservatives. Thus Allen [4] has determined the boric acid naturally existing in many fruits (and in consequence in fermented beverages, such as cider, prepared from them), and has found quantities as great as 0·016 per cent. Desmouliére [5] again has called attention to the existence of traces of salicylic acid in cherries, and thus supplies another example of the somewhat widespread occurrence of that substance in the vegetable kingdom.

Treadwell and Koch [6] deal at some length with the estimation of fluorine in wine and beer, and advocate, in the former case, a modification of Rose's method. For the estimation of boric acid in milk, butter, and other foods, Partheil and Rose [7] recommend a gravimetric method in which the acid is extracted with ether. The question of the detection and identification of artificial colouring matters in articles of food is of considerable importance to the food analyst in view of the ever increasing use of the aniline and other synthetical dyes, some at least of which cannot but be regarded as objectionable for such a purpose. The work of Formánek among others which was undertaken with the object of showing the relation between the constitution of certain dyes and their absorption spectra has incidentally shown that a properly conducted spectroscopic observation may often supply information which cannot well be obtained by any other known method. In this connection, attention may be directed

[1] *Zeit. Nahr. Genussm.*, 1904, **7**, 257; **8**, 227.
[2] *Ibid.*, 389.
[3] *J. Amer. Chem. Soc.*, 1904, **26**, 1086.
[4] *Analyst*, 1904, **29**, 301.
[5] *J. Pharm. Chim.*, 1904, **19**, 212.
[6] *Zeit. anal. Chem.*, 1904, **43**, 469.
[7] *Arch. Pharm.*, 1904, **242**, 477.

to a paper by Onfroy [1] on the identification of the colouring matters in absinthes, since, although based upon methods already known, it may be of use in connection with the examination of some other alcoholic beverages. Much analytical work bearing on the composition and sophistication of well-known drugs has been done during the year, but in many cases the results are scarcely of sufficient general interest, even if space permitted, to justify special reference to them here. Thorpe and Holmes [2] describe a method for the estimation of methyl alcohol in the presence of ethyl alcohol, which is capable of being usefully applied to the detection and approximate estimation of methylated spirit in tinctures and other medicinal preparations. Exception is taken to the B.P. test for cinchonidine in quinine by Paul,[3] who suggests an alternative method, and attention may be called in this connection to a paper by Léger [4] on the determination of quinine in the presence of other cinchona alkaloids. Dowzard [5] has slightly amended the process for the determination of morphine in opium and tincture of opium which he recently proposed as a substitute for the B.P. method, the latter being in his opinion not only clumsy, but inaccurate. While dealing with the analysis of alkaloidal materials, reference may be made to a useful paper by Léger [6] in which methods are given for the assay of nux vomica, Ignatius bean, ipecacuanha, and cinchona bark. Comparatively little advance has been made during the year in connection with the analysis of wines and other fermented beverages. Gugliemetti and Coppetti [7] have suggested a method for the estimation of glycerol in wine, which appears to be a useful modification of the well-known process involving extractions with ether and alcohol. Ley [8] has suggested the application of his zinc precipitation method to the estimation of tartaric acid, Robin [9] details a method for the estimation of citric acid, and Mathieu [10] describes a new process for the estimation of aldehydes. The analytical chemistry of cider vinegar is dealt with in a very useful paper by Leech and Lythgoe.[11]

As a result of a magisterial decision under the Sale of Food and Drugs Acts in connection with the composition of brandy, the analysis of that spirit has received a considerable amount of attention during the past year in this country. The methods adopted have been largely those in use in the Paris Municipal Laboratory, and described in the *Manuel Pratique de l'analyse des alcools et des spiritueux*, by Girard

[1] *J. Pharm. Chim.*, 1904, **19**, 99.
[2] *Trans.*, 1904, **85**, 1.
[3] *Chemist and Druggist*, 1904, **65**, 428.
[4] *J. Pharm. Chim.*, 1904, **19**, 427.
[5] *Pharm. J.*, 1904, **18**, 397.
[6] *J. Pharm. Chim.*, 1904, **19**, 479.
[7] *Ann. Chim. anal.*, 1904, **9**, 11.
[8] *Pharm. Zeit.*, 1904, **49**, 149.
[9] *Ann. Chim. anal.*, 1904, **9**, 453.
[10] *Rev. intern. Falsif.*, 1904, **17**, 43.
[11] *J. Amer. Chem. Soc.*, 1904, **26**, 375.

and Cuniasse. Windisch[1] makes an important contribution to this subject, and interesting articles dealing with the same matter will be found in the *J. Pharm. Chim.*, 1904, **19**, 481 and 593. It is clear, however, that chemical methods alone are at present incapable of indicating with certainty the source or origin of a sample of spirit, or of distinguishing in many cases between the genuine and the carefully prepared factitious article.

In August last the Committee appointed by the Council of the Royal Institute of Public Health to consider the standardisation of methods for the bacterioscopic examination of water issued their Report. This document,[2] suggesting as it does "standard" methods for the collection of samples, the preparation of nutrient media, and the identification of certain specific bacteria, cannot fail to be of considerable interest to all analysts who are called upon to express an opinion on the purity of water.

Apparatus.

Within the limits assigned to this Report it is not possible to refer to all the new pieces of apparatus which have been devised and described during the past year, and the following list therefore contains references to those appliances alone which appear to be most generally useful.

"A simple thermostat for use in connection with the refractometric examination of oils and fats." T. E. Thorpe (*J. Chem. Soc.*, 1904, **85**, 257).

"An instrument for determining the degree of turbidity and depth of colour of solution. (Diaphanometer.)" J. König (*Zeit. Nahr. Genussm.*, 1904, **7**, 129 and 587).

"The nephelometer, an instrument for detecting and estimating opalescent precipitates." T. W. Richards and R. C. Wells (*Amer. Chem. J.*, 1904, **31**, 235).

"Improved gas absorption apparatus." O. Scheur (*Chem. Zeit.*, 1904, **28**, 598) and N. Wolff (*Chem. Zeit.*, 1904, **28**, 644).

"A new lamp for colour matching." W. M. Gardner and A. Dufton (*J. Soc. Chem. Ind.*, 1904, **23**, 598).

"A new fractionating apparatus." J. Houben (*Chem. Zeit.*, 1904, **28**, 525).

"A new explosion pipette." O. Pfeiffer (*Chem. Zeit.*, 1904, **28**, 686).

"A new apparatus for the steam-distillation of small quantities of liquid." Pozzi-Escot (*Bull. Soc chim.*, 1904, **31**, 932).

"A measuring flask with specially graduated neck for the

[1] *Zeit. Nahr. Genussm.*, 1904, **8**, 465.
[2] *Journal of State Medicine*, 1904, August.

preparation of standard solutions." A. Goske (*Chem. Zeit.*, 1904, **28**, 795).

"A shaking and stirring apparatus for use with heated flasks attached to reflux condenser." J. W. Brühl (*Ber.*, 1904, **37**, 918).

"A new double surface condenser." H. E. Burgess (*Chem. News*, 1904, **90**, 249).

"An improved form of Kipp's apparatus." R. J. Friswell (*Chem. News*, 1904, **90**, 154).

"A comparative refractometer scale (slide rule) for use with fats and oils." A. E. Leech and H. C. Lythgoe (*J. Amer. Chem. Soc.*, 1904, **26**, 1193).

"Improved measuring tube for Dumas' nitrogen process." Anton Landsiedl (*Chem. Zeit.*, 1904, **28**, 643).

The greater part of the labour involved in the preparation of this Report has been due to the difficulty of selecting from the very extensive literature of the subject those communications which appear to be most deserving of notice. In a review covering so vast a field it is perhaps too much to hope that errors of judgment have been entirely avoided, and within the limits of this Report it was inevitable that many useful observations should have been left unrecorded. The author has, however, striven to present a *résumé* of the work of the past year, containing references to the more important analytical investigations, and one in which regard has been had not only to scientific merit, but to utility and practical importance.

ALFRED C. CHAPMAN.

PHYSIOLOGICAL CHEMISTRY.

The majority of the abstracts in the Journal of the Chemical Society which deal with subjects of bio-chemical interest have been prepared by me during a period of nearly twenty years. I may, therefore, be pardoned if I preface the first of these Annual Reports by a brief comparison of the condition of physiological chemistry at the present day with what it was some years ago.

If even a superficial survey of modern physiological literature is taken, one is at once struck with the great preponderance of papers and books which have a chemical bearing. Chemistry is coming to be recognised more and more as one of the foundations of physiology, and a mainstay of the art of medicine. From this point of view, the physiological journals of to-day contrast very markedly with those of thirty, twenty, or even ten years ago. The sister science of chemical pathology is making similar rapid strides. When, in 1886, my duties as an abstractor began, there was only one journal (Hoppe-Seyler's *Zeitschrift*) which dealt with chemico-physiological subjects only, and a dozen, or at most twenty, abstracts per month was my output. Now there are several new journals devoted to the subject, and in 1903 a *Centralblatt*, edited by Dr. C. Oppenheimer, dealing with bio-chemistry alone, made its appearance. The number of abstracts prepared each month is seldom under fifty, and usually much exceeds that number. Even then it is only possible to deal with the principal journals, and if time permitted the number might be easily doubled. In some Universities the importance of biological chemistry is recognised by the foundation of chairs which deal with that subject; and, although in the United Kingdom, owing mainly to lack of funds, this aspect of the advance of science is not very evident, there are signs that the date cannot be far distant when every well-equipped University or University College will follow the example set us at many seats of learning on the Continents of Europe and America, and at Liverpool.

Chemical physiology is rapidly becoming a more exact science. I can perfectly well remember the time when those who

devoted their time to the chemical side of biology might almost be counted on the fingers of one hand, and when chemists looked with scarcely veiled contempt on physiological chemistry; they stated that physiologists dealt with messes, impure, non-crystalline materials, and, therefore, anything in the nature of correct knowledge was not possible. There was a good deal of truth in these accusations, and if physiologists to-day cannot say that they have changed all that, they can at least assert with truth that they are changing it. This is due to a growing *rapprochement* between chemists and physiologists. Most of the rising generation of physiologists now go through a thorough preliminary chemical training; and, on the other hand, there is a growing number of pure chemists—of whom Emil Fischer is one of the most eminent—who are recognising the importance of a systematic study of substances of physiological interest. A striking instance of this is seen in the progress of our knowledge of the carbohydrates, which has culminated in the actual synthesis of many members of the sugar group. Another is the accurate information we now possess of the constitution of uric acid. The chemical constitution of proteid or albuminous substances is still for the future. In spite of the overwhelming importance of this subject, the correct knowledge of which underlies so much of vital phenomena, chemists and physiologists long refrained from any attempt to unravel the mystery of the proteid molecule. But, little by little, the puzzle is being solved; many of the proteids have now been crystallised; the simplest proteids, the protamines, are yielding their secrets to Kossel and his co-workers; Emil Fischer has brought his great experience to bear on the problem, and important developments are eagerly expected. When this great conquest of organic chemistry is accomplished, physiologists will be furnished with new light on most of the obscure spots in physiological science. Already one outward and visible sign of the greater exactitude coming over proteid chemistry is seen in the altered position now occupied by abstracts of papers dealing with it in our journal. Such abstracts fill a humble place at the end of the organic chemistry section; they have been elevated from the more outlying districts of Part II.

Before it is possible to attempt a synthesis of the proteid molecule, a preliminary necessity is a correct knowledge of its analytical cleavage products. One of the most instructive methods of accomplishing such cleavage is by means of proteolytic ferments. According to the doctrine of Kühne, peptic as well as tryptic digestion leads to the formation—first of primary albumoses, which are then broken up into secondary albumoses, and these in turn into

the still smaller molecules of peptone. He further differentiated between the peptone produced in the stomach—amphopeptone—and that produced during pancreatic digestion. In the former, two hypothetical groups were still united, of which one—the hemi-group—could be further decomposed by trypsin, whilst the other—the anti-group—was resistant. Tryptic digestion, according to him, thus led to an antipeptone, which differed from amphopeptone in the absence of the hemicomplexes, these having been decomposed with the formation of amino-acids.

These views have been modified by recent investigations. Through the Strasburg school, in particular, it has been shown that the number of primary products of peptic digestion is larger than Kühne supposed, and that in quite early stages in digestion substances are formed alongside of the albumoses which no longer give the biuret reaction, and these have been termed peptoids. The secondary albumoses, which, at a later stage, are derived from the primary, are also numerous; following this, products are formed which differ from the albumoses in the fact that they cannot be precipitated by saturation with ammonium sulphate in either acid, alkaline, or neutral media.

Kühne himself doubted the unity of antipeptone, and it has now been demonstrated that amphopeptone and antipeptone in the original meaning of the words do not exist. These hypothetical substances represent mixtures of various fundamental constituents of the proteid molecule, some of which give the biuret reaction. These products, moreover, are the same whether the decomposition of the molecule is accomplished by pepsin or by trypsin. The essential difference between the two enzymes lies in their velocity of reaction; in this respect trypsin is more active than pepsin.

With the destruction of the original concept of peptone, interest centres in the final products from which the tissue proteids must again be constructed. These comprise the mono-amino-acids, leucine, alanine, glycine, aminovaleric, glutamic, and aspartic acids; the diamino-acids, or hexone bases, arginine, lysine, and histidine; the sulphur-containing substances, cystin; the aromatic amino-acids, tyrosine and phenylalanine, and certain pyrrolidine derivatives. They represent various nuclei which exist preformed in the albuminous molecule, and are linked together in more or less complex groups. The combinations of amino-acids have been named peptides by E. Fischer, and he has shown that substances of this kind are formed during proteolysis and occupy a position intermediate between the albumoses and the end-products. Among the results of tryptic digestion of fibrin, egg-albumin, and other proteids, he has demonstrated the presence of polypeptides at a time

when the amino-acids of which they are composed are also partly present in the free state.[1] How far the primary products of proteolysis are absorbed and contribute to the formation of the protoplasmic proteids is uncertain, but evidence is accumulating to show that both during gastric and intestinal digestion the albuminous molecule is more completely broken down to its fundamental components than was considered to be the case by Kühne and his school. If this is so, the various proteids of the living body must be formed synthetically from comparatively simple substances in a manner quite analogous to the formation of fat and of glycogen. Among others, Löwi has shown that it is possible to maintain nitrogenous equilibrium in dogs by feeding them with the crystalline cleavage products resulting from pancreatic proteolysis which no longer give the biuret reaction, and, although his work has been questioned in some of its details, his main contention appears to have been proved. We are thus presented with an entirely new conception regarding the origin of the most important chemical material of living substance.

I have interpolated this brief account of our new ideas concerning proteids at this point for sake of convenience, but before passing on to the consideration of the literature of the past year, I desire still further to clear the way by noticing some other features which characterise modern researches in the chemical fields of physiology.

The first of these is the increasing importance which physiologists recognise in a study of inorganic chemistry. The importance of water, of oxygen, of various salts and acids need hardly be mentioned. The discovery of argon and its allies in the atmosphere hardly touched physiology at all; whether these elements have any bio-chemical interest is still a question for the future. But with the discovery of radium there is a different story to tell, and the problem whether the emanations from radioactive substances have sufficient penetrative power to make them of real use in the therapeutic sense is attracting world-wide attention. The importance of oxygen for life is one of the truisms of the physiologist. How much he has still to learn about oxidation in the body was amply demonstrated at a discussion on this subject held at the recent meeting of the British Association at Cambridge. The *rôle* of oxygen in the body is not so simple as it is in the ordinary combustion of a candle; for, although oxygen is important in the formation of such products of decomposition as carbon dioxide, it appears to be still more essential in the opposite phase of meta-

[1] On the synthesis of polypeptides, *see* E. Fischer and Suzuki, *Abstr.*, 1904, ii, 771.

bolism, the building up of living materials. It is proverbially more difficult to build up than to destroy, and so it is possible that the agents called oxydases (provisionally grouped with the enzymes) may exercise what influence they possess on this more difficult side of the metabolic process.

The new branch of inorganic chemistry, called physical chemistry, has given us entirely new ideas of the nature of solutions, and the ionic theory is one of fundamental importance in the study of such questions as osmosis. In a brief review of this kind it is impossible to do more than indicate a few of the questions of physiological interest touched by the physical chemist. The old experiments of Ringer on the importance of inorganic salts on contractile tissues have been amply verified, and are now interpreted as due to ionic action. Loeb, Mathews, and their colleagues in America, have gone so far as to consider that the process of fertilisation and the nature of the nerve impulse are to be mainly explained on an electrolytic basis, and up to a certain point have supported their views with experimental evidence. But whether such sweeping and revolutionary ideas will stand the test of further verification cannot be stated with certainty at present. There is always danger that the importance of a new idea may be overestimated; the ionic theory may be a universal cure for all our previous ignorances, but the chances are that it is not. It has its proper place, and an important place, into which it will ultimately settle when the glamour of novelty wears off. At any rate, the mere suggestion that such eminently vital phenomena as excitability, rhythmicality, reproduction, and nervous action are either in whole or in part due to the physical action of inorganic substances indicates the undesirability of postulating the existence of any special mystic "vital force."

It is, however, not correct to speak of physical chemistry as inorganic only. Many eminent chemists consider that the future advance of organic chemistry also will be on the new physical lines. It is impossible to forecast where this will lead us to; suffice it to say that not only physiology, but also pathology, pharmacology, and therapeutics will receive new accessions to knowledge, the importance of which will be enormous. During the past year the last volume of Hamburger's great work [1] on the bearings of a knowledge of osmotic phenomena on medical learning has appeared, and the fact that three large volumes have been necessary to contain a discussion of the questions involved is an index of the rapid growth this aspect of the matter has undergone. Whether proteids

[1] *Osmotischer Druck und Ionenlehre in den med. Wissenschaften.* By H. J. Hamburger. Wiesbaden: J. F. Bergmann. 3 vols

exert osmotic pressure is a moot point with the physiologists; Waymouth Reid answers the question in the negative.[1]

The next general feature which has characterised bio-chemical research, especially during the last few years, is the immense amount of work which has been carried out in connection with theories of immunity. The name of Ehrlich will be immortalised in this connection, and his discoveries bid fair in the future to be reckoned with those of Newton, Darwin, and Pasteur. Whatever may be the fate in the future of his side-chain theory, there can be no doubt that it has been the means of stimulating research and so leading to important discoveries. Without entering into details, the theory may be regarded as an expansion of the *simile* of "lock and key," which Emil Fischer first put forward in relation to ferment action. Bacteriolysins and similar substances are dual bodies, consisting in part of a ferment-like material now known as the complement, and a second substance called the amboceptor which anchors it on to the material to be acted upon.

This work has not advanced yet into the regions of exact chemistry. The substances in question are, doubtless, proteid or proteid-like in their characters. No one has yet seen an antitoxin, a hæmolysin, an agglutinin, a precipitin, and the like in a state of purity, even in solution; but they are there, and it is only a matter of hard work in the future to isolate them successfully. The important discoveries that have centred around this work are not only numerous, but many are of incalculable benefit to mankind. Thus we have been provided with a certain cure for the terrible malady diphtheria, and for that scourge of many tropical climes, snake bite. Various forms of protective inoculation (for plague, typhoid, &c.) have been introduced, although in some cases the matter is still in the experimental stage. We have been furnished with the new biological test for blood, and are so enabled to distinguish the blood of different animals, which the microscope, spectroscope, and chemical testing were previously unable to do. New light has been shed on several obscure physiological questions, especially in regard to ferment action. Ferments are also probably dual bodies. This first became a certainty in relation to Pawlow's discovery of enterokinase. The pancreatic juice, it is now known, contains no trypsin. Claud Bernard, the earliest to examine pancreatic digestion with profitable results, entirely missed its proteolytic action. The substance it contains is the mother substance of trypsin, trypsinogen. When it meets the succus entericus in the intestine, trypsin is liberated, and the result is a powerful proteolytic agent. Pawlow regards enterokinase as itself a ferment, and speaks of it as a

[1] *Abstr.*, 1904, ii, 830.

"ferment of ferments." Delezenne, on the other hand, regards it in the nature of an amboceptor. Starling upholds Pawlow's view with many convincing experimental arguments. Which is right must be left for the present. The discovery of enterokinase has led to the search for, and in some cases to the discovery of, other kinases, and a whole field of exploration as to the action one ferment has on another has been opened up.

Then there is no doubt that there are anti-ferments; we have papers now dealing with antirennet, antipepsin (for example, Ascoli and Bonfanti on antidiastases,[1] Cathcart on antitrypsin [2]) and the like. The old difficulty of why the alimentary canal does not digest itself is thus capable of a rational explanation.

The same ideas underlie recent work on the vexed problem of blood coagulation; Morawitz and others may have introduced some temporary confusion by the coining of new words, but the principle of the new theories is that the thrombin or fibrin-ferment requires for its activity something in the nature of an amboceptor, or a kinase, or both, and that the presence of antithrombin will explain why fibrin-ferment is not always effective in promoting fibrin formation. These are just a few instances to show that the explanations of ferment action and ferment inhibition are becoming intelligible.

The discovery of secretin belongs to the same category of inexact chemistry as that of anti-toxins and anti-ferments, but it is none the less important, and its inexactitude is the fault of its youth, which it will outgrow. A chemical substance is produced owing to the action of acid in the intestine; this substance is absorbed, carried by the blood to the pancreas, and there stimulates the flow of pancreatic juice. This substance is named secretin by its discoverers, Bayliss and Starling; it is an organic substance of comparatively small molecular weight, but that is all we know yet from the chemical point of view. Whether there are other similar secretins concerned in the stimulation of other secretions, such as milk, it is impossible to forecast; but they are being eagerly sought after. For many years we have been too much in the habit of regarding the telegraphic system of the body, the nerves, as the sole means of communication between its various districts; the slower messenger, who is equally useful, the blood, has been rather apt to have the value of its carrying properties underestimated.

If now we turn to the more immediate object of this review, we shall find in the literature of the past year papers illustrating all the general features of progress to which I have devoted the introduction. We shall, moreover, find instances of the extension of

[1] *Abstr.*, 1904, ii, 827. [2] *Ibid.*, 833

chemical work in the elucidation of pathological problems, even in connection with obscure nervous diseases. We shall find similar progress in the region of comparative bio-chemistry, and the branch of physiology called pharmacology looks as though the time will soon arrive when it will be bigger than the parent tree.

It will, of course, be impossible to deal with every paper; those I shall select for comment will only be the most striking, or those of most general interest. It is possible that another writer might have made a different selection, but it will be my endeavour not to allow my personal predilection for certain subjects of research to obtrude itself too forcibly. To reduce the large amount of material to something like order, I shall arrange what I have to say under general headings.

Proteids and their Decomposition Products.

The particular class of proteids which has attracted the special attention of investigators recently is that of the nucleo-proteids; some papers have dealt with their physiological action, others with the more strictly chemical side of the subject. In the former group the work of Prof. MacWilliam[1] deals with the effect of injecting nucleo-proteids intravascularly. The usual effect of such an injection is death, due to intravascular coagulation. Clotting, however, does not occur in blood shut up in an artery or vein; it must, therefore, be in the capillary area that the conditions for inducing fibrin formation are present. On the other hand, it is well known that injections of small amounts of nucleo-proteid lead to what Wooldridge termed the "negative phase," that is, the blood is rendered incoagulable. MacWilliam finds that if the lower half of the body is cut off from the circulation, this does not occur, and suggests that the anti-substances responsible for the negative phase are generated in the abdominal viscera. Another interesting point he noted was that the exophthalmos, which is such a prominent symptom in death from nucleo-proteid injection, is due to hæmorrhage into the orbit.

The quantitative relationships of the blood proteids have formed the subject of several papers; thus Lewinski[2] gives a large number of estimations of the plasma proteids in different animals, and in man under normal and pathological conditions; the effect of various diseases appears to be very slight, and inanition, a condition which certain older observers stated led to a great reduction in the amount of serum-albumin, produces in dogs a very small decrease of this proteid. In experimental infections with the pneumococcus and streptococcus, Langstein and Mayer[3] find a great increase in total

[1] *Abstr.*, 1904, ii, 195. [2] *Ibid.*, 183. [3] *Ibid.*, 184.

proteid, and in the relative amounts of the globulins (fibrinogen and serum globulin).

We must, however, note that the time-honoured classification of albumins and globulins seems in danger of disappearing. The artificiality of the distinction was first mooted by Starke two or three years ago; Moll[1] now states that by simply warming serum to 56—60°, the globulin is increased at the expense of the albumins, hydroxyl ions being regarded as the cause of the change.

The old statement that albumoses are present in normal blood during digestion has been recently reaffirmed by Bergmann and Langstein;[2] they find the quantity, although small, is of appreciable physiological importance. But, as the method adopted did not exclude the possibility of the formation of hydrolytic products, this conclusion should be regarded with caution. Abderhalden and Oppenheimer[3] have arrived at the opposite result

A large number of papers deal with the chemistry of nucleic acid, and the difficulty of this work is accentuated by the numerous acids included under that name. Levene and his colleagues[4] have studied the decomposition of nucleic acid from various organs by various agents; thus, from the nucleic acid of the testis, on hydrolysis with 1 per cent. sulphuric acid, they obtained mainly guanine and adenine; by the use of stronger acid at a high temperature they obtained thymine and cytosine. The purine bases appear to be easily removable by weak acids, the pyrimidine bases are more firmly fixed in the molecule, and require more drastic measures to dislodge them. According to Burian,[5] the purine bases in nucleic acid are combined with phosphoric acid through the nitrogen atom in position 7. These are a few instances of the sort of work now in progress, which will in time result in a knowledge of the constitution of the nucleic acid molecule. At present, however, in spite of the importance of nuclein and nucleates in the composition of the living cell,[6] there is much uncertainty even as regards the empirical formulæ of these substances.[7]

Tryptophan is an instance of a proteid cleavage product in which research has at last definitely made out the constitution. This material in the proteid complex is responsible not merely for the bromine reaction, but also for Adamkiewicz's reaction. Hopkins and Cole, to whom we owe the discovery, assigned to tryptophan the name α-aminoscatoleacetic acid and the formula

$$C_6H_4\begin{<}CMe\\NH-\end{>}C\cdot CH(NH_2)\cdot CO_2H,$$

[1] *Abstr.*, 1904, i, 356. [2] *Ibid.*, ii, 826.
[3] *Ibid.*, ii, 623. [4] *Ibid.*, 1904, i, 126, 955; ii, 498.
[5] *Ibid.*, 1904, i, 358, 956. [6] I. Bang, *ibid.*, ii, 428.
[7] Kostytschew, I. Bang, *ibid.*, i, 127.

but Ellinger has shown that the formula is more probably

$$NH\begin{<}{C_6H_4}{CH}{>}C\cdot CH(CO_2H)\cdot CH_2\cdot NH_2,$$[1]

and that tryptophan is therefore indoleaminopropionic acid Osborne and Harris [2] point out that the intensity of the tryptophan reaction with different proteids indicates that the proportion of this substance yielded by proteids differs considerably. Tryptophan also has been shown to be the parent substance of kynurenic acid (Ellinger), and is, further, the cause of Liebermann's colour test for proteids.[3]

Another product of proteid decomposition, urinary indican, has risen into prominence owing to polemical discussions as to its origin, and the best methods of estimating it.[4] There seems, however, but little doubt that tryptophan is an intermediate stage in the formation of indican. Monfet [5] attributes Ehrlich's diazo-reaction in urine to indican, but this is apparently a mistake.[6]

Polemics have also centred around the ureine of W. O. Moor.[7] This author maintains that the urea of the urine amounts to only one-half, or even less, of what is usually stated to be the case, the other half of the nitrogen being contained in this new substance called ureine. Ureine seems destined to fall into the list of forgotten materials. Among other investigators, Gies [8] points out that it is a mere mixture of different organic and (mainly) inorganic constituents of the urine; urochrome forms a large proportion of the organic constituents present.[9]

Hæmoglobin.—A most interesting and suggestive piece of work on blood pigments has been carried out by P. P. Laidlaw.[10] He has shown that even dilute acids in the absence of oxygen will lead to the formation, not of hæmatin, but of hæmatoporphyrin. The fact that oxygen confers stability on the iron of the blood pigment had been previously pointed out by Hoppe-Seyler, although this was denied by Nencki and Sieber. By quite simple treatment, the iron may be replaced in hæmatoporphyrin, and hæmatin is thus synthetically obtained. If copper is similarly introduced into the hæmatoporphyrin, a pigment is obtained having all the characters of turacin, the red pigment of the feathers of the plantain-eating birds.

[1] *Abstr.*, 1904, i 639. [2] *Ibid.*, 125. [3] Cole, *ibid.*, ii, 103.
[4] Hervieux, *ibid.* 63; Bouma, *ibid.*, 102; Monfet, *ibid.*, 63, 102; Maillard, *ibid.* 193; Underhill, *ibid.*, 193 754 Rosenfeld, *ibid.*, 193; Salkowski, *ibid.*, 753.
[5] *Ibid.*, 63, 194. [6] Maillard, *ibid.*, 194.
[7] *Ibid.*, 192, 274. [8] *Ibid.*, 192. [9] Haskins, *ibid.*, 754.
[10] *Ibid.*, i, 1067.

Enzymes.

General.—The action of electrolytes on ferments has been the subject of a paper by Cole.[1] Anions other than those of hydroxyl accelerate, whilst cathions and hydroxyl ions retard, the activity of amylolytic ferments. We may place in the same category the work of Arrhenius[2] on the physical chemistry of agglutinins, which shows how the results published previously by Eisenberg and Volk may be employed quantitatively.

The combined action of ferments is a branch of research opened up by Pawlow's discovery of enterokinase. For many years previous to this, however, Schiff and Herzen had insisted on the importance of the spleen in promoting the efficiency of pancreatic action. The experiments of Levene and Stookey[3] corroborate the view that the spleen facilitates the transformation of trypsinogen into the active enzyme. They were unable to detect any similar action of the spleen on the liver.

The most striking statement in the same direction has been Cohnheim's announcement that the pancreas facilitates the combustion of sugar in the muscles. If this occurs within the body as the result of an internal secretion of the pancreas, we are provided with an explanation of the diabetes that follows extirpation of that organ. The active substance in the pancreas, which is responsible for this action, was at first placed among the ferments, but more extended experiments have shown that the material in question is not destroyed by heat, and is soluble in alcohol.[4] The same, or a similar material, is present in the blood also.

The lipase of the liver has been shown by Magnus[5] to consist of two substances; one, the ferment, is not dialysable and is destroyed by heat; the other, the "co-ferment," is dialysable and is not destroyed by boiling. Cohnheim's substance from the pancreas is very similar to Magnus's co-ferment.

These facts point to the possibility of the nature of ferment action being elucidated more fully in the future. Ferments are subtle substances, evading the search of the chemist to a large extent, but if the co-ferments are definite chemical materials soluble in alcohol there is hope that their nature will be speedily determined, and so the nature of their more evasive partners is likely to be made clearer at the same time. In the same way, the idea that lecithin is one of the materials concerned in the efficient action of snake venom holds out promise of corresponding enlightenment.[6] Similar experi-

[1] *Abstr.*, 1904, i, 131. [2] *Ibid.*, ii, 356. [3] *Ibid.*, 674.
[4] *Ibid.*, 675. [5] *Ibid.*, 628.
[6] Preston Kyes, *ibid.*, 431.

ments by Wells, in order to determine whether thyroid, kidney, and spleen influence the autolytic digestion of the liver, led to negative results.[1] The action of pepsin upon itself has been stated[2] to lead to the formation of peptone. If this is so, pepsin is a proteid.

Velocity of Reaction.—The study of the velocity of enzyme reactions is rapidly making the subject amenable to exact and mathematical treatment. An important series of papers on this aspect of the problem is at present appearing in the *Proceedings of the Royal Society* by E. F. Armstrong and Caldwell.[3] We have here an excellent example of how that *rapprochement* between chemical and physiological study, to which I have already alluded, is bearing important fruit. The numbers given show that enzymes are more active than acids in promoting hydrolysis, but this apparent activity is due to the greater affinity the enzyme has for the sugar, and that in reality the acid has the greater hydrolytic activity.

Blood Coagulation.—The cause of blood clotting has been a vexed question ever since physiology became a science, and still remains so. As explained in the introductory portion of this article, a new note has, however, been recently struck in relation to the matter, and Morawitz has, in particular, advanced the view that thrombin or fibrin-ferment is not a single substance. The α- and β-thrombins, as he terms its two components, have each precursors, α- and β-prothrombin, and matters are still further complicated by the presence of antithrombin.[4] The principal new idea introduced is that a kinase analogous to Pawlow's enterokinase is necessary to effect the change of the prothrombins into thrombins in addition to calcium ions.[5] Fuld and Spiro[6] have used mainly birds' blood plasma in their work, and on the lines of the new theory seek to explain the effect of muscle extracts, leech extract, peptone, and other agents which hinder or promote coagulation, as the case may be. The complexity of the subject has not been made less intense by the introduction of a number of new terms (cytozyme, plasmozyme, holozyme, &c.); but this is a usual symptom of the embryonic condition of new theories.

Another worker at blood-clotting is Leo Loeb; he has studied the subject from the comparative point of view;[7] the so-called first coagulation in arthropod blood is an agglutination of corpuscles, analogous to that of blood-platelets in vertebrate blood; this is followed by true fibrin formation. Agglutination and fibrin formation are in all cases separate phenomena;[8] the action of

[1] *Abstr.*, 1904, ii, 574.
[2] Herlitzka, *ibid.*, 828.
[3] *Ibid.*, i, 956—958, 1070.
[4] *Ibid.*, ii, 59.
[5] *Ibid.*, 353.
[6] *Ibid.*, 353.
[7] *Ibid.*, 353.
[8] *Ibid.*, 496.

tissue extracts in promoting coagulation is regarded as being due to specific substances called coagulins, and not to adherent lymph.

Erepsin.—This is an enzyme, first described by Cohnheim, in the dog's succus entericus, which has the power of splitting peptones into simpler products, although it has no action on the native proteids. It is also present in the succus entericus of herbivora.[1] At first Cohnheim attributed great importance to this ferment, but Kutscher considers it is comparatively feeble and unimportant. Starling, in this country, uses the term erepsin for the feeble proteolytic ferment which is contained in many animal tissues; it is, for instance, present in fresh pancreatic juice, and is quite distinct from trypsin. Our knowledge of pancreatic erepsin has been increased by work performed by Vernon.[2]

Autolysis.—A very large amount of work is now being devoted to this subject. The following are the principal papers:—Hedin, on proteolytic enzymes of spleen and serum;[3] Levene, on autodigestion of liver and pancreas,[4] and of testis and spleen;[5] Arnheim, on the favouring action of gelatin and carbohydrates on the autodigestion of the liver;[6] W. Jones, on the autodigestion of thymus and suprarenal;[7] Kutscher and Lohmann, on the end-products of pancreatic autodigestion;[8] Lane-Claypon and Schryver, on the stages noticed in the progress of autolysis;[9] and W. Jones, on autodigestion of nucleo-proteids.[10] There can be no doubt that the activity manifested by so many workers is warranted by the importance of the subject. The tissue enzymes are important in the metabolic cycle during life, and before it is possible to state what those functions are it is obviously necessary to study what happens when the ferments are allowed full scope after death. The curious thing about such enzymes is, that the majority act best in an acid medium, whereas the healthy tissues during life are alkaline. There can, however, be but little doubt that there are temporary phases of acidity, or acid foci in living cells, although the reaction of a mass of the tissue to the ordinary indicators may be alkaline. There is, further, no doubt that the nuclei of cells are the main centres for nutritional exchange, and so especial interest attaches to the results of autolysis of nucleo-proteids. Here it is found that the end-products often differ markedly from those which result from hydrolysis by acids, and so Jones and Partridge[11] searched for and found certain specific enzymes which account for the difference. Fresh pancreas when subjected to autolysis does not yield adenine or guanine, and guanine when added to it is transformed rapidly into xanthine; the name *guanase* is bestowed

[1] Nakayama, *Abstr.*, 1904, ii, 425. [2] *Ibid.*, 57. [3] *Ibid*, 58.
[4] *Ibid.*, 188. [5] *Ibid.*, 574. [6] *Ibid.*, 189. [7] *Ibid.*, 191.
[8] *Ibid.*, 425. [9] *Ibid.*, 574. [10] *Ibid.*, 625. [11] *Ibid.*, 838.

on the enzyme to which this change is due. Guanase is also present in thymus and kidney, but not in spleen. Spleen contains an enzyme *adenase*, which, in a similar way, converts adenine into hypoxanthine.

The search for such ferments acting on comparatively simple materials was no doubt the direct result of the suggestive work of Kossel and Dakin, which led them to the discovery of *arginase*. This discovery is certainly one of the most striking and important of the whole year's work in physiological chemistry. Arginase [1] splits arginine almost quantitatively into urea and ornithine. The failure of some observers to find arginine in the products of the autodigestion of organs is due to the previously unsuspected action of arginase, which must now be placed among Richet's urea-forming ferments. Arginase is found in the intestinal mucous membrane, but more especially in the liver; nerves, thymus, and lymph glands are also active, but blood and muscles have practically no such action.[2]

We therefore see that the study of autolysis has already had the important practical issue of enabling us to obtain a little deeper insight into the metabolic processes that lead to urea formation.

Immunity and Allied Problems.

This is becoming a vast subject, with an extensive literature of its own. I have already attempted to indicate its importance, but seeing how much has yet to be done to bring the subject within the region of exact chemistry, the abstracts that have appeared do not do much more than touch the fringe of the matter.

At the recent meeting of the British Medical Association, at Oxford, a most instructive discussion was held in the Section of Pathology on immunity and the questions related to it, and I cannot do better than recommend those interested in the subject to read the account of that discussion published in the *British Medical Journal* of September 10th, 1904.[3] All I shall attempt here is to call attention to some of the more important points noted in the papers abstracted for the Journal of the Chemical Society.

Venoms and Antitoxins.—Elliott, in conjunction with Sillar and with Fraser,[4] has added to our knowledge of the action of the venoms of the krait and of the sea snakes. In both cases Calmette's serum has no protective or curative value. W. H.

[1] *Abstr.*, 1904, ii, 425, 840.

[2] See also Levene on hydrolysis of fresh and self-digested glands, *ibid.*, 828.

[3] Pp. 557 *et seq.* See also Bordet on "Chemical Theories of Immunity," *Abstr.*, 1904, ii, 832.

[4] *Abstr.*, 1904, ii, 630.

Wilson [1] has furnished interesting facts concerning the mode of action of the venom of the scorpion. The tissue mainly affected is the muscular tissue, and the effect produced resembles that caused by veratrine. Desert animals likely to come in contact with scorpions possess natural immunity against their poison, the resistance of the Jerboa being 300 times greater than that of the guinea-pig. Curiously enough, however, the excised muscles of such animals are as readily affected by the venom as those of animals which are not immune.

Coming nearer home, it may be a relief to those who suffer from pollen poisoning or hay fever to know that an antitoxin has been prepared against this ailment, and that it gives excellent results.[2] A paper on the power of the liver to destroy diphtheria toxin [3] should also be mentioned.

Agglutinins.—Gengou [4] and Gerard-Mangin and Henri [5] have worked at the subject of agglutination produced by various chemical reagents. G. N. Stewart [6] has made a very thorough study of the subject, and not the least interesting of his results is that corpuscles fixed by formaldehyde nevertheless cause on injection a production of specific agglutinins, and to a less extent of hæmolysins also; and, further, that such corpuscles are themselves agglutinated by specific sera.

Precipitins.—Kraus and Levaditi [7] discuss the origin of these substances, and conclude that they are produced mainly by the leucocytes. The most striking paper, however, is one by L. Moll,[8] who has a conception of precipitins diametrically opposed to that of most other authorities on the subject. According to him, the proteid of the immune serum is the passive reagent; the precipitin it contains is the substance precipitated; precipitin and precipitate are related to one another in the same way as fibrinogen and fibrin. The whole precipitin question, and the results of the examination of thousands of specimens of blood will be found most ably discussed in a recent book by G. H. F. Nuttall.[9]

Blood and Respiration.

Apart from the subject of coagulation, which we have already considered, the number of papers on the blood has not been great. There has been some discussion on whether glycerol exists in the blood, a by no means unimportant point with regard to fat meta-

[1] *Abstr.*, 1904, ii, 630. [2] Glegg, *ibid.*, 578.
[3] Brunton and Bokenham, *ibid.*, 832. [4] *Ibid.*, 496. [5] *Ibid.*
Ibid., 497. [7] *Ibid.*, 423. [8] *Ibid.*, 184.
[9] *Blood Immunity.* Cambridge University Press. 1904.

bolism. Nicloux maintains that it is present, whilst Mouneyrat disputes the accuracy of Nicloux's methods.[1]

Locke has improved his methods for keeping the excised mammalian heart alive with oxygenated Ringer's solution, and demonstrated the important effect which sugar has in increasing its efficiency; of the sugars used, dextrose alone has any action in this direction, and evidence is adduced of the disappearance of part of the dextrose after some hours' activity.[2] Hering and Gross[3] have carried out somewhat similar experiments, and their results confirm those published many years ago by Ringer in connection with the frog's heart, results which Loeb has shown are to be interpreted as due to the action of ions.

We may place in the same category with these the researches of Zoethout on the effect of salts on muscular tissues, and on what Loeb has termed "contact irritability";[4] of Lillie on the relation of ions to ciliary movement;[5] and of Row on the effects of Ringer's fluid on plain muscle, which are much the same as on skeletal and heart muscle.[6] Müller and Ott[7] have made attempts to resuscitate the brain of animals by oxygenated salt solutions, as Locke, Kuliabko, and others have done with the heart, but failed. When the supply of blood to the brain ceases, the grey cortex rapidly undergoes chemical changes, which cause it to react acid to litmus. The importance of a continual stream of arterial blood is familiar to all, a slight diminution in the supply causing unconsciousness.

Experiments on respiration have been mainly limited to those on the effects of altered atmospheric pressure. We now know that caisson disease is due to too rapid "decompression," and the consequent liberation of gas bubbles in the blood.[8] Work on the opposite question, the effect of rarefied air on the blood and respiration, has been mainly stimulated by Mosso's labours in his Monte Rosa laboratory.[9] The chief result of this work has been to confirm, often with fresh details, the older observations that the diminution of pressure must be considerable to produce harmful or even detectable results, and that the principal effect on the blood is an increase of the corpuscular elements. The sensitiveness of the nervous system to the action of alcohol is diminished at great altitudes.

In this connection we must not omit to mention the important work which Beddard, Pembrey, and Spriggs have commenced on the gases of the blood during diabetes and diabetic coma;[10] they have

[1] *Abstr.*, 1904, ii, 56, 270. [2] *Ibid.*, 422. [3] *Ibid.*, 55. [4] *Ibid.*, 190.
[5] *Ibid.*, 273. [6] *Ibid.*, 190. [7] *Ibid.*, 627. [8] L. Hill, *ibid.*, 54.
[9] Mosso, *ibid.*, 622, 757; Kemp, *ibid.*, 183; Bartlett, *ibid.*, 54; Durig, *ibid.*, 270; Tissot, *ibid.*, 495. [10] *Ibid.*, 622.

already shown that our ideas concerning the cause of diabetic coma will need revision.

The part played by oxygen in the tissues is a moot point, and has been so for a long time in connection with muscle. Similar questions have arisen in connection with secreting glands and nervous tissues. Baas,[1] working in Verworn's laboratory, has shown, in confirmation of Baeyer and Fröhlich, that oxygen is necessary for the continued activity of excised nerves, and that normal nerves in the body probably participate in respiratory metabolism. The idea is not new, for Waller some years ago brought forward circumstantial evidence in favour of the view that nerves produce carbon dioxide when in action.

A paper which I find difficult to classify is Macallum's, on the Palæochemistry of the Ocean, but as I have alluded to the inorganic salts of the blood in this section, I place a brief notice of it here. The paper ought to be carefully read, and even the long abstract I gave of it[2] hardly does it justice. In the blood plasma of vertebrates, the relationship of sodium, potassium, and calcium is strikingly like that which now obtains in sea-water; magnesium, however, is present in smaller proportion. This is due to heredity, and reproduces the condition of the sea-water at the date when a circulatory system first appeared. If it were possible to determine the proportion of the four elements in protoplasm, good grounds are adduced for believing that their proportion would be that which obtained in sea-water in more distant ages before the development of the circulation.

Digestion and Metabolism.

In connection with digestion, the pancreas still maintains the interest that the discovery of secretin stimulated. In Starling's laboratory, de Zilwa[3] has examined the composition of the juice obtained by secretin and by pilocarpine. In the former case, the alkalinity is greater, but the total solids and the proteids are less in amount. Bainbridge,[4] working in the same place, has directed renewed attention to what is called the adaptation of the pancreas. Weinland was the first to show that, on a milk diet, the pancreas rises to the occasion by producing lactase; according to Bainbridge, this is chemical adaptation, the lactose acting on the intestinal mucosa in such a way as to produce a material which, after absorption, stimulates the pancreas to produce an unaccustomed enzyme. Glaessner[5] has had the unusual opportunity of examining human

[1] *Abstr.*, 1904, ii, 576. [2] *Ibid.*, 495. [3] *Ibid.*, 574.
[4] *Ibid.*, 424. [5] *Ibid.*, 270.

pancreatic juice, and confirms the work of Pawlow and others who have mainly worked with the juice obtained from animals, with regard to the times of maximal secretion, and the necessity of its being activated by the intestinal juice. The increased oxygen absorption that accompanies pancreatic activity has been demonstrated by Barcroft and Starling.[1]

General Metabolism.—Atwater and his colleagues in Connecticut continue their monumental labours in the collection of statistics.[2] Another centre of activity on metabolic work in America is the Yale Laboratory, presided over by Prof. Chittenden. The long-established idea that a man requires a minimum of 15 grams of nitrogen in his daily food is being seriously questioned; Chittenden himself and his colleagues have maintained their health and equilibrium on much less.[3] It is, however, too early to state yet whether such deprivation will have any harmful effects. This question was taken up originally by Mr. Horace Fletcher, who is stated to have cured himself of dyspeptic and other troubles by lessening his proteid nutriment below what was regarded as the physiological standard, and has started a propaganda on the subject from the economic point of view; but in France two observers, Labbé and Morchoisne,[4] have even gone beyond Fletcher by subsisting on a proteid intake of only 2 to 3 grams daily for thirty-eight days. They state their health remained good all the time, but the tables they publish show a loss of body weight. Succi and other fasting men also stated they felt pretty well after no nutriment at all for forty days.

Rubner, another prominent investigator in the metabolic field, has done yeoman service in proving that the law of the conservation of energy holds good for the chemistry of living things; he was the earliest to draw prominent attention to the necessity of an investigation of the fæces, as well as of the other excreta in the construction of accurate metabolic balance-sheets. Among his followers, Lohrisch,[5] in estimating the energy of the dejecta by means of calorimetry, invariably found their heat value was greater than that reckoned from their chemical composition; this is, however, capable of a simple explanation, namely, that at present errors of analysis arise in the examination of such a complex mixture as fæces; for instance, it is incorrect to consider that the ethereal extract is all fat; it also contains lecithin and cholesterol. The purine substances in fæces have been estimated by Walker Hall;[6] and Rockwood[7] confirms the statement previously made by Burian that the endogenous uric acid differs in different individuals, but

[1] *Abstr.*, 1904, i, 827. [2] *Ibid.*, 186.
[3] *Physiological Economy in Nutrition.* By R. H. Chittenden. New York: F. A. Slater and Co. 1904. [4] *Abstr.*, 1904, ii, 498. [5] *Ibid.*, 428.
[6] *Ibid.*, 358. [7] *Ibid.*, 673.

remains remarkably constant, even on different diets in the same person.

Glycogen.—Pflüger's Archiv in general, and Pflüger himself in particular, continue to pour forth voluminous papers on this subject. A welcome exception to this rule is to be found in an admirably concise article by Pflüger, which gives the main steps in the new method of estimating glycogen, originally introduced by Pavy, by means of strong potash.[1] This new method has rendered most of the older estimations of glycogen in organs useless, and by it this substance has now been detected in many places where its existence was previously unsuspected. Analytical details regarding the amount in the fœtal liver have appeared during the year.[2] Loeschcke [3] states that glycogen is free, not chemically bound in the organs where it occurs, and the chemical and physical properties of absolutely pure glycogen have been described by Gatin-Gruzewska.[4]

The Cerebro-spinal Fluid.—The phosphorised fat of the nervous system was originally described by Liebreich as protagon; Hoppe-Seyler denied the chemical individuality of this substance; Gamgee resuscitated it; Baumstark and Kossel supported Gamgee; and lately Thierfelder and Lesem and Gies gave it what they considered its death blow. Cramer [5] has, however, again revived it, and shown that it has a perfectly constant composition. It is, moreover, one of the few substances from the brain that can be obtained in a definite crystalline form. Its molecule, however, is too heavy to contain more than a small fraction of the phosphorus of the nerve fat, and no one denies that the bulk of the phosphorus is contained in the smaller molecules of lecithin, kephalin, and other phosphorised components.[6] All these substances resemble one another, and resemble proteids in being in that condition of unstable chemical equilibrium we term metabolism; and all, moreover, yield among their decomposition products the alkaloidal material, choline. In various nervous diseases, the presence of choline in the cerebro-spinal fluid and blood is an indication of organic breakdown; katabolism exceeds anabolism. In nervous diseases which are termed functional, no such evidence of decay is forthcoming. Hence, in difficult cases of diagnosis, the test for choline comes to the aid of the practical physician, as Mott and I were the first to point out. In Germany the question has been taken up by Donath, who has confirmed our results, but somewhat modified the test with platinic chloride, on which he places most reliance.[7] He also finds that,

[1] *Abstr.*, 1904, ii, 595. [2] Pflüger, *ibid.*, 427. [3] *Ibid.*, 576.
[4] *Ibid.*, i, 838. [5] *Ibid.*, 462.
[6] For recent quantitative work, *see* W. Koch, *Abstr.*, 1904, ii, 498.
[7] *Ibid.*, 63.

with the decomposition of phosphorised fats, the amount of phosphates rises in the cerebro-spinal fluid.[1] In America similar results have been obtained by Dana and Hastings,[2] and in his latest paper, Donath quotes several other confirmatory observations. There have, on the other hand, been some investigators who appear as critics; Mansfield's statement,[3] that the crystals obtained by Donath are simply due to inorganic chlorides, has been amply refuted by Donath;[4] Allen, who, in conjunction with French, began as a doubter,[5] has later become a convert to the true faith;[6] he, however, regards the test with iodine, with the modifications he has introduced, as more trustworthy than the test made with platinic chloride.

Pharmacology.

The number of papers relating to the physiological action of drugs is almost as great as the number of drugs, and the term Pharmacology includes also the action of other chemical and physical agents on the living organism. In the greater number of cases, I fear, I must adopt the subterfuge of referring inquirers to the forthcoming index (*Trans.*, 1904); all I can attempt to do here is to allude to a few of the most prominent or interesting of the agents investigated.

Among those recently discovered, the Röntgen rays and radium have attracted considerable attention. W. B. Cannon[7] has continued his useful work on digestion by means of Röntgen ray shadows, and by mixing the food with bismuth has been able to estimate the rate of discharge from the stomach into the intestines. His main conclusion is that acid in the stomach is the great stimulus for the opening of the pyloric orifice, and in the intestine for its closure.

So much was hoped for at first in the direction of cure of cancer, &c., by means of these rays, that it is important to call attention to their danger; the skin irritation caused by constant exposure to the rays sometimes leads to the formation of cancer, and, as in the case of Edison's assistant, may thus be fatal.

Radium emanations may be found curative in the future; up to the present, investigators have mainly succeeded in demonstrating their injurious effects. The penetrative power of the emanations through the skin appears to be slight, so there is little hope of employing them for the destruction of micro-organisms or other agents that set up deep-seated disease. The principal papers on the physiological effects of radium have been the following during the

[1] *Abstr.*, 1904, ii, 628. [2] *Ibid.*, 359. [3] *Ibid.*, 623. [4] *Ibid.*, 791.
[5] *Ibid.*, 100. [6] *Ibid.*, 623. [7] *Ibid.*, 189.

year—Henri and Mayer,[1] who show that the emanations alter the osmotic properties of blood corpuscles and change hæmoglobin into methæmoglobin; Bonchard, Curie, and Balthazard,[2] who have demonstrated the fatal effects of air charged with the emanations in mice and guinea-pigs; after death the tissues, especially of the surface, are radioactive. Salomonsen and Dreyer[3] killed animalcules by exposure to the emanations. A. B. Green[4] performed similar experiments with vegetable micro-organisms, and these also after exposure show marked signs of radioactivity.

We may next select a couple of examples from agents which have been known longer, and which still continue to excite controversy, namely, alcohol and chloroform.

That alcohol is a food within certain limits may now be accepted as a proved fact, whatever view may be taken as to the advisability of its habitual use. This has been shown by Atwater in America, and by Rosemann in Germany, the last of whose painstaking researches has recently been published.[5] Another controversial point frequently cropping up in connection with alcohol is whether or not it is in small amount found in normal animal tissues. Landsberg[6] supports the view that it is. The proportion in which it occurs is stated to be from 1 in 11,000 to 1 in 33,000 parts. The source of the alcohol is uncertain; unless bacterial action occurs, it is not increased by digesting the tissues with sugar.

In reference to chloroform, one may allude to the important discussion opened by Sir Victor Horsley at the Oxford meeting of the British Medical Association, in which the majority of the leading physiologists and anæsthetists of the country took part.[7] Although the speakers differed as to the best form of apparatus to use, Vernon Harcourt's and Dubois's being those most discussed, it is satisfactory to find that all agreed that 2 per cent. of chloroform vapour in the air is all that is necessary, and that beyond this proportion danger lies. Dr. Waller, who has been specially instrumental in forcing this conclusion on anæsthetists, has introduced a simple densimetric method of estimating chloroform.[8] Perhaps the most interesting contribution to the chloroform question from the chemical point of view is that by Moore and Roaf.[9] They point out that all living cells are subject to anæsthesia, although, of course, most attention is generally directed to the units of the nervous system. The action must, therefore, take place between the anæsthetic and some chemical substance present in all varieties of protoplasm, and theories based on the high content of nerve-cells in lecithin and fatty constituents may be disregarded. Proteid is the material of

[1] *Abstr.*, 1904, ii, 184. [2] *Ibid.*, 502. [3] *Ibid.*, 577. [4] *Ibid.*, 503.
[5] *Ibid.*, 187. See also Goddard, *ibid.*, 827, for similar experiments on dogs.
[6] *Ibid.*, 499. [7] *Ibid.*, 756. [8] *Ibid.*, 622. [9] *Ibid.*, 501.

all others universally present, and it is found that chloroform forms loose compounds with many proteids; if in excess, it will precipitate some of them. This explains the greater solubility of chloroform in blood, or serum, or hæmoglobin solutions, than in water or in saline solutions. The loose compound of proteid-chloroform is compared to oxyhæmoglobin. When anæsthesia occurs the proteid-chloroform compound of the blood has parted with its chloroform to the cell-proteids. The compound there formed undergoes dissociation when the chloroform pressure is reduced on cessation of administration of the anæsthetic, and anæsthesia thus ceases.

The substance of all others which has produced the largest number of pharmacological papers has been adrenaline. The work has not been wholly pharmacological, but much has been done from the purely chemical side also. It is not remarkable that adrenaline (epinephrine) should have excited all this interest, for it is one of the most powerful physiological agents that are known. The small doses of the homœopathists are gigantic as compared to those of adrenaline, which are capable of producing distinct physiological results.

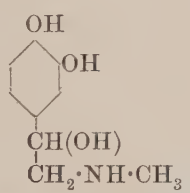
I will take the work relating to physiological action first. Loeper [1] finds that adrenaline produces hæmolysis and stimulates the blood-producing organs; Doyen and Kareff [2] that it leads to diminution of the glycogen of the liver, and increase of the sugar in the blood; Exner [3] that it lessens absorption, and so, after its administration, other poisons like strychnine produce death more slowly; Meltzer [4] that it causes the pupil to dilate in the frog in all circumstances, but in the mammal only after section of the cervical sympathetic nerve. Hamburger [5] has studied the antagonism on blood pressure between it and "peptone" injected intravenously. The question has been discussed by Embden and von Fürth,[6] by Weiss and Harris,[7] and by others, as to what becomes of it after injection. The view has been advanced that it is destroyed in the muscles; Embden and von Fürth consider that it is destroyed in the blood, but this is not confirmed by Weiss and Harris, who find that the blood of an animal poisoned with the drug, but which has become "accustomed" to the effect, is still capable of producing a rise of blood pressure when injected into another animal. Brodie and Dixon [8] have conclusively proved that adrenaline acts on sympathetic nerve-endings, not on the muscular fibres where these terminate. This idea has been developed by T. R. Elliott,[9] who postulates the necessity for the presence of adrenaline in any effective sympathetic action, and has shown that it

[1] *Abstr.*, 1904, ii, 196. [2] *Ibid.*, 272. [3] *Ibid.*, 276. [4] *Ibid.*, 560, 632
[5] *Ibid.*, 501. [6] *Ibid.*, 61. [7] *Ibid.*, 628. [8] *Ibid.*, 66, 196.
[9] *Ibid.*, 577.

is produced also in the sympathetic ganglia; all embryologists know the close developmental association between the medulla of the suprarenal gland and the sympathetic nervous system. The same author has also worked out the action of adrenaline on the bladder.[1] Important as most of these conclusions are, they pale in interest when one comes to the chemical side of the investigation. For, not only has the empirical formula of adrenaline been made out, but also its constitution has been determined. The actual synthesis of adrenaline has not yet been accomplished, but this culmination of the work cannot be far off, for already a ketonic derivative (adrenalone) has been synthesised, but its power to elevate arterial pressure is much inferior to that of adrenaline. Abel in America and von Fürth in Strassburg have long been struggling with this question, and it is curious that neither of them has the credit of the final discovery, although it was their work which paved the way to it. The priority of the synthesis of adrenalone is now being disputed between Friedländer[2] and Stolz.[3]

The formula for adrenaline is one of two originally suggested by Pauly[4] and confirmed by Jowett.[5] Other papers which have appeared on the question are those by Abderhalden and Bergell,[6] and by Bertrand.[7]

The formula in question is



and adrenaline is thus a methylamino-derivative of catechol.

In the introduction to this article I have drawn attention to the greater exactitude which is characterising the work of modern physiological chemists, and it is most fitting to conclude the review by a brief description of this marked instance of useful results following a combination of study of a subject from both the physiological and the chemical points of view.

W. D. Halliburton.

[1] *Abstr.*, 1904, ii, 832.
[2] *Beitr. chem. Physiol. Path.*, 1904 **6** 92.
[3] See Hans Meyer, *Centralblatt. Physiol.*, 1904, **18**, 501 ; *Abstr.*, 1904, i, 1069.
[4] *Abstr.*, 1904, i, 128, 540.
[5] *Trans.*, 1904, **85**, 192.
[6] *Abstr.*, 1904, i, 791.
[7] *Ibid.*, 956.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

Although Agriculture is the oldest of the arts, yet the application of chemistry and allied sciences to it is of but comparatively recent growth. It is only natural, therefore, that inquiry should have been directed in the past mainly to the explanation of facts and processes observed in the practice of agriculture rather than to any subversion of the methods employed in an industry of such antiquity. But the progress of recent inquiry would seem to be aiming at some revolution in the methods of practice also, and the record for the year 1904 bears evidence of this.

At the same time, it can hardly be said that the year has been marked by any startling discovery, by any epoch-making contribution to our knowledge, or by many events of exceptional interest. Under the last head may, however, be mentioned the issue of the Report of the fifth "Internationaler Kongress für angewandte Chemie," held in Berlin, June 2nd—8th, 1903, vol. III. of this report including the Proceedings of Section VII. (Agricultural Chemistry).

The year's Obituary is, happily, a short one, the loss, however, of Dr. A. P. Aitken—who died on April 17th—claiming attention and calling forth expression of regret. For the long term of twenty-seven years Dr. Aitken had occupied the position of chemist to the Highland and Agricultural Society of Scotland, and was well known in this connection and as a professional chemist in Edinburgh. He was a frequent contributor, on chemico-agricultural subjects, to the Highland Society's Journal, and was Director of their Agricultural Station.

The outstanding features of the year may be briefly summarised as follows:—In so far as "discovery" may be spoken of, one may record (1) the application of cyanamide to agricultural purposes, and (2) the improvement and adaptation of "nitragin," or similar nitrogen-inoculating materials, may be recorded. As regards the lines upon which inquiry has mainly proceeded in different countries, it may be said generally that, alike in England, Germany, and America, attention has been chiefly directed to questions con-

cerning nitrification and the utilisation of atmospheric nitrogen, while, in England and America chiefly, workers have been also largely occupied with problems bearing upon the mechanical division and physical condition of soils in relation to their agricultural value. Further, the consideration of the "available" constituents of soils and of the best means of determining these has engaged much thought in all three countries. In Germany, in particular, the behaviour of farmyard manure, either in respect of the losses it undergoes in making and storage, or of the changes effected in presence of nitrates applied along with it, has been the subject of continued study. Coming to individual soil-constituents, numerous points connected with the existence of an insufficiency of lime and its suitable supply, as also of the inter-relations of lime and magnesia as found in soils, and the bearings of these on practice, have provided a fruitful field of labour. Green-manuring, in its relation to the "atmospheric nitrogen" theory, has been pursued both at Rothamsted and at Woburn, and a new branch of inquiry has been opened up in the study of the influence of minute applications of some of the less abundant materials met with in agriculture, such as manganese. Work in this branch was commenced at Woburn in 1898, and has been continued since, the record for 1904 comprising the results of observations not only from this station, but from Germany and also from Japan.

In the domain of Vegetable Physiology, more particularly, the prominent feature has been the great amount of work done, and the advance in our knowledge of the enzymes and of their action. Towards this, much service has been rendered in particular by the able contributions of Prof. Vines, Dr. Horace Brown, and Dr. E. F. Armstrong.

The appearance in 1904 of the first part of the Transactions of the Guinness Research Laboratory[1] (under the direction of Dr. Horace Brown) has been, indeed, welcomed as the first of a series of systematic investigations into the nature of barley and the changes which it undergoes in the germinative process. Prof. Vines's discourse before the Linnean Society, on "Proteid Digestion in Animals and Plants,"[2] also did much to put on a clear basis the results of past investigations on this subject.

Coming to more strictly agricultural matters, mention should be made of the papers contributed to the Chemical Society of London by Mr. A. D. Hall, director of the Rothamsted Experimental Station, on "Mechanical Analysis of Soils,"[3] and by Mr. S. F. Ashby on "The Comparative Nitrifying Power of Soils";[4] and of

[1] *Trans. Guinness Research Lab.*, 1903.
[2] *Linnean Soc.*, published minutes, December 1, 1904.
[3] *Trans.*, 1904, **85**, 950.
[4] *Ibid.*, 1158.

the contributions to the "International Congress" by Prof. A. Frank, "Die Nutzbarmachung des freien Stickstoffes der Luft für Landwirthschaft," [1] and Dr. L. Hiltner, "Die Impfung der Leguminosen mit Reinkulturen." [2]

A pleasing feature of the year has been the renewal of activity in connection with the "Rothamsted Experiments," made famous by the works of Lawes and Gilbert, and with this has come, under the care of the new director, Mr. A. D. Hall, a welcome popularising of the work of the station with a view to making it better known to, and its lessons better understood by, the practical farmer. Already, in 1903 and 1904, have appeared in the Journal of the Royal Agricultural Society of England, papers dealing with the continuous experiments on mangels [3] and on permanent grass,[4] and others are in process of preparation. Further, while the historical labours of Lawes and Gilbert have been maintained in their integrity and the continuity of the records been preserved, the scope of the work has been extended so as to embrace inquiries into matters of more recent moment, and others bearing in some respects more directly upon farm practice.

Cyanamide.

To deal now in more detail with the principal points comprised in the year's work, we take first the production of cyanamide and its application to agricultural purposes as a means of utilising the nitrogen of the atmosphere and converting it into plant food. Frank, of Charlottenburg, gives in the paper to which reference has just been made, and which was read at the International Congress in Berlin, an account of his work on this subject, describing how, in conjunction with Caro, he had observed the taking up of nitrogen by the carbides of the alkalis and alkaline earths formed in the electric furnace. They experimented with the carbides of barium and calcium in particular, the latter being found the most applicable, inasmuch as the taking up of nitrogen by calcium carbide produced, not calcium cyanide, but a separation of carbon and formation of calcium cyanamide ($CaC_2 + 2N = CaCN_2 + C$). From this compound, by the interaction of water, ammonia would be formed ($CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$). This substance could also be produced by heating lime or chalk with charcoal at 2000° in a current of air. The product calcium cyanamide is sold in Germany commercially under the name "Kalkstickstoff," and contains from 14 to 22 per cent. of nitrogen, according to its varied method of pre-

[1] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 727.
[2] *Ibid.*, 799.
[3] *J. Roy. Agric. Soc.*, 1902, **63**, 27.
[4] *Ibid.*, 1903, **64**, 76.

paration. It remained to put it to the test for agricultural purposes, and this was done by Wagner at Darmstadt and Gerlach at Posen, both by pot-culture trials and in the field, and with results that betokened success, it being stated that the effect of the cyanamide fell very little short of that produced by salts of ammonia containing the like quantity of nitrogen. The nitrogen of the calcium cyanamide is changed into ammonia in the soil, and this then undergoes nitrification. Although these favourable accounts of its use have been set out, it is evident that the material must be put more thoroughly to the test before a definite pronouncement can be made. In 1904, a field trial with it was undertaken at Rothamsted, in comparison with ammonium sulphate, but without any very definite result. In Germany, the field trials were never as successful as those with pot-culture, and there was evidence that with some soils, especially those of peaty nature, there was an injurious action. This is attributed to the formation of dicyanodiamide by the action of acids. Takke [1] states that a poisonous action was observed when the material was added just before sowing the seed, but not when an interval of two and a half months was allowed to elapse. It is evident, however, that, even if proved useful agriculturally, the success of cyanamide as a commercial enterprise must depend entirely upon the cheap production of electric energy, as where water-power is available.

Nitragin.

Nitragin was originally brought out by Nobbe, of Tharand, and Hiltner in 1896, but, as is well known, it failed in its original form. Since then efforts have been made to reproduce it in better form, it being felt that the underlying principle in its preparation and use was correct and consistent with the discoveries made by Hellriegel. It was believed that the failure of the "nitragin," as at first produced, was due to the bacteria dying for want of suitable food before the seed germinated, or, possibly, to the bacteria being injured by secretions from the seed itself in its early stages of germination. These defects Hiltner (now of Munich) and Störmer have sought to remedy by supplying nourishment for the bacteria in the form of grape sugar and peptones added to the water used for the inoculation and cultivating them in this.[2] Still better than water, they recommended the use of milk. They have made many trials of the nitragin thus prepared, and on different soils, and they maintain that a large measure of success has been obtained, the experiments giving about 78 per cent. of successes with serradella, 75 per cent. with red clover, and 57 per cent. with lupins. Inocula-

[1] *Bied. Centr.*, 1904, **33**, 583; from *Mitt. Ver. Förd. Moorkultur*, 1903, **23**, 347.

[2] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 799.

tion of soil, Hiltner points out, is only suitable in the case of peat land.

Still more recently, G. Moore,[1] of the Plant Physiology Laboratory, U.S. Department of Agriculture, has introduced another method of preparing nitragin. He holds that the failure in Nobbe's case was owing to the medium used for conveying the bacteria being too rich in nitrogen, and so he aimed at giving them only just nitrogen enough. His next step was to secure a simple means of distribution, and, after showing by experiments that the bacteria grown on nitrogen-free media retained their activity for a long time if carefully dried out and subsequently revived in a liquid medium, he used an absorbent, such as cotton, in which form he distributed the material for use, sending it out in packets consisting of the cotton with its dried germs. Along with this go two other packets, comprising the food by which the farmer is to multiply the germs. The first packet contains granulated sugar, potassium phosphate, and magnesium sulphate, and the second ammonium phosphate. The contents of the first packet are dissolved in water, the dried germs (on cotton) added, and the whole left for twenty-four hours in a warm place. The ammonium phosphate is then added, and the mixture again left for twenty-four hours, after which it is ready for moistening the seed and thus inoculating it. Soil may be similarly inoculated. Statements are given of promising results obtained from the treatment, but it is evident that both this preparation and the new one of Hiltner's will have to be very carefully and thoroughly tested in this country before one can be assured of their practical application.

Influence of Nitrates in the Soil on the Action of Nodule Bacteria.

Nobbe and Richter[2] experimented with *Vicia villosa* grown in pots with sand and garden soil, and found that when the pots were inoculated with a pure culture of the *Vicia* nodule bacteria, if sodium nitrate (0·5 gram and 1 gram respectively per pot) was added, the effect of inoculation was distinctly diminished.

Nitrification.

Boullanger and Massol[3] carried out experiments on the action of the nitrous and nitric organisms on ammonium salts. They found that with the nitrous organism in presence of ammonium sulphate there was a period of about six days during which no nitrification

[1] *Century Magazine* October, 1904, **68**, 835.
[2] *Landw. Versuchs-Stat.*, 1903, **59**, 167.
[3] *Ann. Inst. Pasteur*, 1904, **18**, 181.

proceeded; with the nitric organism this lasted only two days. Further, that ammonium salts hindered the multiplication of the nitric organism, but did not, unless present in considerable amount, retard the functions of nitric organisms already existing.

Fausto Sestini[1] finds that the production of nitrous acid in the soil does not arise, as has been stated, from the action of bacteria on atmospheric nitrogen, nor, as believed by Bonnema, is it due to the oxidation of the atmospheric nitrogen by ferric oxide in the soil, but to the presence of the traces of ammonia in the air, which then become oxidised, forming food for the nitric bacteria.

S. F. Ashby[2] has devised a method for the estimation of the nitrifying power of different soils, with the object of comparing their activity in this respect, and thus obtaining a measure of their fertility. This work was carried out in connection with the Rothamsted experiments, and the soils with which the trials were made were those the history of which is well known. After attempting in vain to inoculate sterilised solutions in the field with small quantities of fresh soil taken, with a sterilised spatula, from the sides of a hole, and also by the employment of aqueous extracts of soil, Ashby used hollow brass cylinders, fitting loosely into glass tubes, stoppered with an india-rubber disc. These tubes were previously sterilised. A hole was dug in the soil, and one of the brass cylinders inserted at a depth of 10 cm. from the surface, and driven horizontally into the soil, after which the core of soil withdrawn was transferred to one of the sterilised glass tubes. This was taken to the laboratory, and, after breaking up, was placed over sulphuric acid under a bell jar, which was then partially exhausted. The drying lasted for 48 hours, the soil was next sieved and well mixed, 0·2 gram of it being then seeded into a sterilised solution and incubated at 29—30°. The culture solution was that employed by Wiley: potassium dihydrogen phosphate, 1 gram; magnesium sulphate, 0·5 gram; ammonium sulphate, 0·2 gram; calcium chloride, trace; distilled water, 1 litre. It was found that nitrate formation proceeded well, and there was no evidence of loss from denitrification. Duplicates from different holes on the same plot were found to agree well, and the results as regards the relative nitrifying power were in accordance with what might have been expected from the history of the treatment of the various plots tried, and from a consideration of their crop production. Attempts to shorten the period of incubation by the use of stronger culture solutions resulted in loss of ammonia. Difficulty was experienced in expressing the "nitrifying power" in absolute values, or in terms of so much nitrogen nitrified per litre per day, Ashby finding that during the first fortnight of incubation (the whole period was

[1] *L'Orosi*, 1904, **27**, 1.

[2] *Trans.*, 1904, **85**, 1158.

30—37 days) no trace of nitrite or nitrate was obtained; when, however, the process was once started, it went rapidly, and in a 30 days' incubation it was during the last two days that nitrification really occurred. Ashby proposes to consider the percentage of "total nitrogen nitrified" during an equal period as giving the best comparison of "nitrifying power."

E. J. Russell (an account of whose work has not as yet been published) has devised a method for finding the total "bacterial action" of a soil, and for using this as an index of soil fertility. His plan is to ascertain the rate at which oxygen is absorbed, and he has applied this to various samples of soils from Rothamsted and Woburn, as well as from Wye College, Kent. The method is to put the soil in a flask provided with a side bulb containing caustic potash and a delivery tube leading into mercury, and so serving as a gauge. The flask is put into a bath at 16—18°. As oxygen is absorbed, the carbon dioxide produced is taken up by the caustic potash and the mercury rises in the gauge, giving thus the rate of oxidation, and, presumably, the measure of the total aërobic bacterial activity, which is, no doubt, closely related to the fertility of the soil. The method, as applied to the soil of different plots and fields of the Woburn Experimental Farm, certainly succeeded in placing them in the order of their respective fertility, and Dr. Russell states that this has been the case elsewhere. This method undoubtedly holds out much hope of being practically useful.

Denitrification.

Gaspare Ampola and Celso Ulpiani[1] have continued their cultivation experiments on this subject; these confirm previous observations, and the authors conclude that calcium nitrate, formed as the natural product of nitrification, is, in ordinary circumstances, but slightly attacked by denitrifying bacteria. But, in order to avoid loss of nitrogen, fresh stable manure with much straw should not be applied to the ground during the period of active nitrification; moreover, sodium nitrate, to be used to best advantage, should be applied when the stable manure is thoroughly broken down. This, it may be observed, is fully in accord with the experience of farming practice.

Green-manuring.

The practical application of the principles inculcated by the researches of Hellriegel has, in England at least, not met with the success that might have been expected of them. If it be the case that leguminous crops have the power of utilising the nitrogen of

[1] *Gazzetta*, 1903, **33**, 125—129.

the atmosphere, then it would seem an easy matter to enrich soils in respect of nitrogen by the growing of leguminous crops on them. So far, however, as this has been tried, the results are not in accordance with theory. At Woburn, where this point has been tried continuously since 1892,[1] no benefit has resulted to the succeeding corn crop from the growing and ploughing-in (green) of a leguminous crop, such as tares (vetches), as compared with that of a non-leguminous one such as mustard. The mustard crop has each time produced a better corn crop following its growth and ploughing-in than have the tares, and this whether the green crops had no manuring or were supplied with mineral manures in the form of superphosphate and kainit. It was found, moreover, that the tares supplied to the soil considerably larger amounts both of organic matter and of nitrogen than did the mustard, but there was no corresponding increase in the corn crop, either with wheat or barley. In 1904, lest it might be said that the accumulated nitrogen had not had time to become available, a spring crop (barley) was taken after the wheat crop of the year previous, but even with this there was no better result from the tares than from the mustard. There may be conditions militating against this experiment turning out in accordance with what one would expect from theoretical considerations, and the matter is under further investigation, but at present, at all events, theory does not appear to be borne out in practice, at least so far as the tares crop is concerned. A series of experiments bearing on this same subject was instituted in 1904 at Rothamsted, where also the influence of different clovers is being further investigated in continuation of the researches of Lawes and Gilbert. It is well, however, to point out that until the teachings of theory can be shown in practical application under the ordinary conditions of farming, there can be little hope of their successful incorporation in our agricultural system. Incidentally, too, light is thrown on the need of supplementing pot-culture experiments by others on a field scale.

Soil and Soil-constituents.

As noted previously, a great deal of attention has been directed, and very rightly so, to the consideration of soils in regard to their physical condition and state of mechanical division. In America Whitney and Cameron, and in England A. D. Hall, in particular, have been very active. The American school, however, as represented by Whitney and Cameron,[2] have gone so far as to declare

[1] *J. Roy. Agric. Soc.*, 1903, **64**, 335.

[2] *U.S. Dept. of Agric., Bureau of Soils*, No. 22, "The Chemistry of the Soil as related to Crop Production." By M. Whitney and F. K. Cameron.

that the chemical analysis of a soil has little to do with or to tell about the fertility of a soil, and that fertilisers, if they have any effect in increasing a crop, do so mainly by reason of their altering the physical texture of the soil, or by stimulating the root range of the plant. Whitney and Cameron express themselves dissatisfied with the want of any correspondence between crop production and the results of soil analysis as obtained by the action on the soil of either weak or strong acids, and they take instead the aqueous solution obtained by shaking up 100 grams of soil with $\frac{1}{2}$ litre of water, then allowing this to stand for twenty minutes. This solution is examined by various colorimetric methods for getting rapidly quantitative estimations. As the outcome of this procedure, which, it must be pointed out, has no correspondence whatever with what takes place naturally in the soil, they came to the conclusion "that, with occasional exceptions, the composition of the soil solution and the concentration is about the same in all cultivable soils." They conclude, therefore, that all soils are amply supplied with the necessary mineral plant foods, these not being in themselves of importance except so far as concerns the supply of soil moisture. Such a position as that taken up by Dr. Whitney and his colleague must, indeed, be startling to any student of agricultural chemistry in this country who has had before him the long-continued experiments at Rothamsted and elsewhere, and Mr. A. D. Hall[1] was not slow to show the utter untenableness of the views enunciated. He pointed out that the theory could be disproved, even from the figures quoted by the authors, both as regards the formation of nitrates in the soil and the phosphoric acid contents, quoting also instances from the Rothamsted experiments in support of his argument. As Mr. Hall says, whatever may be the case in America, where much of the land is new and has only recently been brought under cultivation necessitating the use of fertilisers, Dr. Whitney, although right in his main contention as to the water content and temperature of soils being main factors in crop production, has been too ready to ignore the vast body of knowledge accumulated in this country concerning the requirements of particular crops for particular fertilising ingredients, and hence has been led to attribute no importance to the chemical composition of the soil, which, nevertheless, still remains a large factor.

Soluble Salts in Soil.

Other investigators in America, and notably King,[2] have been working at the distribution of soluble salts in soils in their relation to the solid and gaseous components of the soil, and as supplying

[1] *Nature*, 1903, **69**, 58, "A New Theory of the Soil."

[2] *Wis. Agric. Exper. Stat. Reports*, "Soluble Salts of Cultivated Soils."

nutriment to the plant. A number of papers have been written also in regard to alkaline soils, and Hilgard [1] has summarised his several years' work on this subject

Soil Acidity.

On the other hand, soil acidity has claimed considerable attention both in America and in England. F. P. Veitch [2] has made a comparison of the different methods of estimating soil acidity, and the lime-water method introduced by him is recommended. In England the question of soil acidity has derived considerable importance from the exceptional results found at the Woburn Experimental Farm [3] as the outcome of growing continuously wheat and barley crops on the same land—a light sandy loam, poor in lime—and manuring these year by year with ammonium salts (ammonium sulphate and chloride). The continued use of these salts has brought about absolute failure of the crop and the production of an acid condition of the soil, the nature of which is now under investigation. This acid condition, it is found, is remedied by the application of lime to the land, and healthy crops are again produced. The acidity itself is removed by continued washing with water, and also to some extent by exposure to air alone. Following on this, investigations are in progress at Woburn in reference to the relative action of water and of solutions of ammonium sulphate, ammonium chloride, and sodium nitrate on the soil, and to the rate of removal of organic matter, lime, and other constituents therefrom. These show, so far, that the removal of lime proceeds more rapidly with all the above salts than with water, that it is more rapid with ammonium chloride than with ammonium sulphate, and that both these salts take out the lime nearly twice as quickly as does sodium nitrate. Side by side with these results have been obtained interesting ones regarding the mechanical action of the above salts on the soil, to which reference will be made later.

Availability of Soil-constituents.

The question of the availability of soil-constituents and the best methods of ascertaining this continues to be a prominent one, and in England, Germany, and America alike many investigations have been made. Emmerling,[4] summarising his experience of different methods, recommends for the determination of phosphoric acid a

[1] *California Agric. Exper. Stat., Bulletin* No. 128, "Nature, Value, and Utilisation of Alkali Lands."

[2] *J. Amer. Chem. Soc.*, 1904, **26**, 637.

[3] *J. Roy. Agric. Soc.*, 1903, **64**, 355.

[4] *Ber. V. Inter. Kongress für angewandte Chemie*, 1903, **3**, 733.

2 per cent. solution of citric acid, and for lime Kellner's suggestion of boiling in a concentrated solution of sal-ammoniac. H. Ingle [1] has shown that after extracting a soil for seven days with a 1 per cent. solution of citric acid, it is rendered much less fertile, especially at first; but that gradually, during the growth of the plants, chemical changes in the soil render it capable of again supplying plant food. He hence holds that while B. Dyer's method of determining the "available" plant food in soils is very valuable, it is necessary to take into consideration also the rate at which this available plant food is capable of being renewed, and he hints that whilst this may be much the same for soils under similar climatic conditions, it may vary much when tropical or sub-tropical soils are considered.

Ash of Plants and Analysis of Soils.

The difficulties connected with the interpretation of soil analyses have led to some revival of the old idea of the ash of plants being the best guide to the proper manuring of the plant. This has been worked at by Heinrich, Helmkampf, Atterberg, and others, and A. D. Hall,[2] in a paper read at the British Association at Cambridge (1904), reverts to the subject. An examination of data accumulated from the Rothamsted experiments shows that with cereal crops, when the whole plant is taken into consideration, the composition of the grain fluctuates but little with the manuring, and the range of variations shown by the plant is less than that indicated by soil analysis. But with root crops, analysis of the ash indicates a much wider range of variation where manuring with phosphoric acid or potash has given distinct response in the crop, and in these cases the analysis of the ash shows promise of affording a better guide to the requirements of the soil than does the analysis of the soil itself.

Mechanical Analysis of Soil.

The mechanical analysis of soils has received further attention in this country, and in a paper contributed to the Chemical Society A. D. Hall [3] has dealt with a number of soils taken from experimental plots of different fields at Rothamsted. Adopting Schloesing's method of a preliminary treatment of a soil with dilute acid followed by ammonia, he has divided the soil into separate fractions, using the method of sedimentation recommended by Osborne, which consists in dividing the soil into two fractions by sieving and five by sedimentation from water. Hall found that there was rarely obtained

[1] *Trans.*, 1905, **87**, 43, "The Available Plant Food in Soils."

[2] *Brit. Assoc. Report*, 1904. Section K. Sub-section of Agriculture. "Analysis of the Soil by means of the Plant."

[3] *Trans.*, 1904, **85**, 950.

as much of the finest fraction by the sieving of the raw soil as there was when the soil was treated preliminarily with acid. When variations were found, these occurred in the case of soils rich in humus, inasmuch as the humates, which probably acted as a binding material, were decomposed by the acid treatment. The acid treatment has the further advantage of removing all soluble salts which would interfere with the sedimentation. He therefore concludes in favour of the preliminary treatment with acid. Determinations of alumina, silica, and ferric oxide are given in the various fractions separated by the mechanical analysis, and it is shown that, although the alumina increases as the particles become smaller, it is the size rather than the chemical composition of the particles that determines what the fractions are.

Influence of Soluble Salts on the Condition of Soil.

A further paper by A. D. Hall, in the same Journal,[1] deals with the effect produced on soil by the continued application to it of sodium nitrate. Again the Rothamsted plots are brought into use, and an examination of some on which sodium nitrate has been used for a long series of years, when compared with others where none had been applied, shows that in the former case the finer particles are washed down into the subsoil. This was most marked in the case of the mangel field, where cultivation had gone on continuously, whereas, on the grass plots, where there had been no stirring of the surface, this loss of the finer particles was not found. Mechanical analyses of the subsoils from cultivated land, where sodium nitrate has been used continuously, showed them to be much richer in the finer particles than where no nitrate had been applied, and Hall concludes that this is due, not to any solvent action of the nitrate, but to the "deflocculating" action of this salt and subsequent washing of the finer particles into the subsoil. This receives confirmation from experiments already noted at Woburn, where the relative actions of sodium nitrate and ammonium salts on the soil were compared (see page 201). On removing the soils from the cylinders (2 feet long) in which they had been subjected to continued washing with solutions of the salts, it was found that at the bottom of the sodium nitrate cylinder there was a closely aggregated mass of the finer particles, the texture of the soil being quite different to that of the soil in the other cylinders. This mass had, no doubt, been formed in the way indicated by Hall, the finer particles having been carried down to the subsoil.

[1] *Trans.*, 1904, **85**, 964.

The "Rarer" Constituents of the Soil.

The influence on plant life of those constituents of the soil which, because of their rarer occurrence or presence in but small amount, have been less studied, has recently been brought into some prominence both in this country and elsewhere. In 1896 Mr. E. H. Hills, whose attention had been directed to the earlier work of Prince Salm-Horstmar, left a bequest for the purpose of carrying on inquiries on the influence of the "rarer forms of ash" on plants, and out of this the Woburn Pot-culture Station was founded. Since its opening, in 1898, experiments in the direction indicated have been carried on, and have been reported in successive issues of the *Journal* of the Royal Agricultural Society of England. The last published account [1] deals with the action of the iodides and oxides of manganese, potassium, sodium, and lithium on wheat and barley. The iodides generally have proved harmful, even when applied at the rate of 1 cwt. per acre, but the oxides have in each case been beneficial. Lithium salts have had a retarding effect at first upon germination, and the oxide further produced a mechanical change in the soil, causing it to "cake." Water-culture experiments carried on at the same time with barley showed distinct differences in the nature of the root produced with the iodides and oxides respectively, that with iodides being thin and delicate, with one long tap root and but few side shoots, whereas with the oxides there was formation of a short, thick tap root and abundant rootlets and fine hairs.

Previous experiments at the Woburn Station [2] have dealt with the influence of other "rarer" constituents, such as fluorine, chlorine, bromine, and titanium, in addition to iodine, manganese, and lithium mentioned above, and among other methods tried was that of soaking the seed, *before* sowing, in solutions of salts containing these substances. This preliminary soaking of the seed, whereby but small quantities of the constituents are taken up, seems to promise results of much interest, and the work is now being carried on further. Indeed, this would appear to be the line which future study should take with these "rarer forms of ash," namely, the influence of minute quantities of them rather than the application of manurial dressings. Meantime, this work has claimed attention in other countries. O. Loew [3] found that small amounts of manganese sulphate gave an increased yield in the case of different

[1] *J. Roy. Agric. Soc.*, 1904, **65**, 306.

[2] *J. Roy. Agric. Soc.*, 1900, **61**, 567; 1901, **62**, 317; 1902, **63**, 346; 1903, **64**, 348.

[3] *Bied. Centr.*, 1904 **33**, 91; from *Landw. Jahrb.*, 1903, **32**, 437.

families of cultivated plants, cruciferous plants, in particular, being more benefited than the *Gramineæ*. Experiments with rice gave not only increased yield of corn, but more grain to straw as the result of using manganese salts. Sodium fluoride and potassium iodide, similarly used in small doses, increased the yield of oats and peas, as did also uranyl nitrate. Loew subsequently went to Japan, and there continued his investigations,[1] trying, among other things, the effect of manganese sulphate on trees; *Cryptomeria japonica* he found to be doubled in weight in eighteen months. Sodium chloride, on the other hand, reduced the growth. Other workers at Tōkyō have carried on investigations in the same line. K. Asō[2] found an increase of one-third in rice production from an application of manganese chloride. Y. Fukutome[3] showed that the joint application of iron and manganese affected the yield of flax favourably, and M. Nakamura[4] similarly experimented with zinc sulphate, nickel sulphate, and cobalt nitrate in small quantities on *Allium*, *Brassica Chinensis*, and barley, noticing slightly stimulating effects in most cases, although nickel and zinc proved hurtful to barley. Gabriel Bertrand,[5] of Paris, in a paper read before the International Congress at Berlin, 1903, speaks of the necessity of considering other constituents of the soil than those which one usually takes into account, and refers to his own published work on the part which manganese plays in the action of the oxydases. Later on in the discussion he referred to the work of Asō, quoted above, and to the latter's observation that applications of manganese salts, while at first favourable to vegetation, might become hurtful after a certain proportion was reached.

Organic Matter in Soil.

F. K. Cameron and J. F. Breazeale,[6] after comparing different methods for the determination of organic matter in soils, give preference to that of oxidation by means of chromic acid, using 10 grams of soil with 5—10 grams of potassium dichromate, and then concentrated sulphuric acid added gradually. The organic matter is taken as being the weight of $CO_2 \times 0{\cdot}471$. Slight modifications are required in presence of chlorides or carbonates.

[1] *Bull. Coll. Agr. Tōkyō*, 1904, **6**, 126.
[2] *Ibid.*, 131.
[3] *Ibid.*, 136.
[4] *Ibid.*, 147.
[5] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 839, "Les Engrais complémentaires."
[6] *J. Amer. Chem. Soc.*, 1904, **26**, 29.

Fertilisers and their Influence.

Farmyard and Organic Manures.

The making and storing of farmyard manure continues to exercise a great deal of interest among scientific inquirers in Germany. The work on this subject is very well summarised by W. Somerville [1] in his address at the British Association meeting, Cambridge, 1904, and Schneidewind,[2] of Halle, dealt also with it in a paper read at the International Congress in Berlin, 1903. Schneidewind, after discussing the various methods suggested for conserving the nitrogen in farmyard manure, shows that they one and all have drawbacks attaching to their use, and comes to the conclusion—already well established by experimental inquiry and practical experience in England—that there is no plan so good as that of making the dung in deep pits, or boxes, with the use of litter (in Germany usually peat-moss with loamy earth thrown over), the stock treading the manure down and so keeping it moist and firmly consolidated, it being then left to accumulate until ready for removal.

The increasing supply of residues rich in potassium salts, from distilleries where molasses and similar substances are used, has led to these being incorporated with peat to form a "humo-potassic" manure,[3] or these alkali salts may be used in conjunction with peat, previously rendered alkaline, and insoluble phosphates in order to form a humo-phosphatic manure.

Organic substances are believed to exert a solvent action on minerals; this view has received confirmation from experiments by A. Stalström,[4] who thinks that the action is dependent on biological activity. Thus he finds that while sterile organic substances have no solvent action whatever on tricalcium phosphate, yet when the fermentation set up (according to the nature of the organic substance) is of the lactic or butyric kind (as with milk, milk-sugar, or peat with milk-sugar) there is a marked action, but when an ammonia or carbon dioxide fermentation is produced (as with peat, dung, &c.) it is much less marked.

Lime.

The influence of lime on the other constituents of the soil, and the importance of having a sufficiency of it present in a soil, have

[1] *Brit. Assoc. Report*, 1904, **12**. Sub-section K.

[2] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 794, "Die Behandlung und Wirkung des Stalldüngers."

[3] *Fr. Pat.*, August, 1903, 338, 981.

[4] *Centr. Bakt. Par.*, 1904, **11**, 724.

always been recognised alike in practical agriculture and in agricultural science.

The increasing cost of lime has, however, conduced much to the neglect of the good old practice of liming land, and this has incidentally brought out some very valuable points regarding the effect of the continued use of ammonium salts on soils naturally poor in lime. Of these the soil of the Woburn Experimental Farm [1] furnishes a typical example, being a light sandy loam, on the lower greensand formation, and containing about 0·25 per cent. of lime (CaO). For twenty-seven years plots on which wheat and barley, respectively, have been grown year after year, have been dressed each season with ammonium salts (ammonium sulphate and chloride), either alone or in conjunction with mineral manures (superphosphate and sulphates of potassium, sodium, and magnesium). For the first twenty years there was no failure of crop, but after that time there began a decline, more rapid with barley than with wheat, and ultimately entire sterility of the land and an acid condition of the soil were produced (see page 201). This was corrected at once by the application of a dressing of lime (two tons per acre), and good crops were again obtained, the influence of the lime telling for the next seven years. These experiments have led to the further investigations noted on page 201 on the rate of removal of lime from the soil, and the changes produced by ammoniacal and other salts. The importance of lime as a constituent of agricultural soils was further emphasised by H. Immendorff, of Jena,[2] in a paper read at the International Congress at Berlin, in which he speaks of the influence which lime has in rendering both natural and artificial fertilisers effective. He refers further to the presence in certain moorland soils of a lime-compound, or, rather, group of compounds, which he calls "humussäure kalk." These soils, although they contain in the dried state 2 per cent. or more of calcium oxide, yet have frequently no trace of calcium carbonate; the presence, however, of these "lime-humus" compounds ensures to the plants abundant lime for many years to come. For the ready determination of available lime, Immendorff recommends Kellner's method of extraction with sal-ammoniac solution.

While lime is of such importance, it has been shown, however, that excess of it is not desirable, and many experiments have turned upon the relations of the contents of lime and magnesia which it is desirable to have in soils. Loew [3] has pointed out, for instance, that

[1] *J. Roy. Agric. Soc.*, 1903, **64**, 329 and 355.

[2] *Ber. V. Inter. Kongress für angewandte Chemie, Berlin*, 1903, **3**, 736, "Die Kalkbedürftigkeit der Kulturboden und ihre Bestimmung."

[3] *U.S. Dept. Agr. Bur. Plant Ind., Bull.* No. 1, "The Relation of Lime and Magnesia to Plant Growth."

there is a definite ratio of lime to magnesia which should exist in the soil in order to produce the best results with any one plant, and that this ratio differs for different plants, excess of either constituent doing harm. A moderate amount of lime is advantageous, but an excess does harm; lime salts counteract the injurious action of magnesia, and allow the latter to act as a plant food. Loew puts the best relation of CaO : MgO at about 1 for most cereals, whereas with other crops, especially the more leafy ones, twice or three times as much lime is needed.

K. Asō [1] found the lime factor for rice to be about 1, but the yield of rice was less diminished by an excess of magnesia than by a similar one of lime.

R. Ulbricht,[2] experimenting with vetches on a soil containing only small amounts of lime and magnesia, found that lime in moderate amount increased the yield, but reduced it when in excess. Heavy applications of dolomite also were injurious. With potatoes,[3] lime and marl increased the yield of tubers and of dry matter in the tubers, but increased the yield of leaf more than that of the tubers. In the absence of lime there was least phosphoric acid in the leaf, but with lime present the amount of potash in the leaf was increased. In the tubers there was little difference as regards the phosphoric acid and potash, as the result of applying or withholding lime. As more magnesia was applied the leaves were found to contain less calcium, but the tubers were not affected in this way.

The influence of lime on phosphates used in conjunction with it has also been studied. H. Bachmann [4] found that lime and basic slag used together increased the yield of rye (grain), but not that of oats (grain), and lime with phosphoric acid increased the beet crop. B. Schulze's [5] experiments on the influence of lime on bone-meal show that the benefit of the phosphoric acid of the bone-meal varies according to the time of liming, it being least when the two are applied together in spring, and greater when the lime is applied in autumn and the bone-meal in spring, but that bone-meal and lime should not be applied to the same crop. Schulze attributes the diminution of crop to the action of the lime on the phosphoric acid of the soil, which becomes thereby difficultly soluble. The organic acids in the soil are likewise neutralised and their solvent action lost.

[1] *Bull. Coll. Agr. Tōkyō*, 1904, **6**, 97.
[2] *Landw. Versuchs-Stat.*, 1904, **60**, 135.
[3] *Ibid.*, 1903, **59**, 1.
[4] *Bied. Centr.*, 1903, **32**, 801—803
[5] *Chem. Zeit.*, 1904, **28**, 158.

Phosphates.

The search for further supplies of phosphatic materials continues, and during 1904 new rock deposits of calcium phosphate have been found in Tunis and in South Australia. The former are in the district of Uarfa-Tarf, analysis showing an average of 63 per cent. of calcium phosphate, with 14—20 per cent. of calcium carbonate and 1·5 per cent. of alumina; the latter on Yorke peninsula, whence samples have given calcium phosphate varying from 70 to 83 per cent.

Solubility of Phosphates.

Several new processes have been introduced for making the phosphoric acid in raw phosphates soluble for manurial purposes. Among these is one by A. Ystgaard,[1] in which powdered apatite is fused with carnallite for 10—15 minutes at 700—800°, the following reaction taking place:—$Ca_3P_2O_8 + 3MgCl_2 = Mg_3P_2O_8 + 3CaCl_2$. The product, which is easily pulverised, contains 80 per cent. of its phosphoric acid soluble in a 2 per cent. citric acid solution. A mixture of 100 parts of apatite, 200 of carnallite, and 100 of kieserite will yield, after lixiviation with cold water, a product with more than 20 per cent. of phosphoric acid and 7 per cent. of potash. Experiments with this material have shown that it gives better results than basic slag.

Nitre which has been washed, or a hot aqueous solution of sodium bisulphate, has been used [2] to act on calcium phosphate so as to obtain the greater part of the phosphate in a form in which it is soluble in water or in citrate solution. Wolters [3] has fused together compounds of silicic acid with neutral or basic compounds of phosphoric acid, and then suddenly cooled the product. The phosphates are found to be readily soluble in citric acid. The same may be produced by mixing natural phosphates with silicates previously prepared by the fusion of sand with alkalis. P. Wagner [4] has prepared "Wolter phosphate" by fusing together a mixture of 100 parts of crushed phosphorite, 70 parts of sodium bisulphate, 20 parts of calcium carbonate, 22 parts of sand, and 6—7 parts of coal. The product is poured into cold water and, after drying, is finely ground. Of the phosphate, 97 per cent. was found to be soluble in citric acid solution, and in vegetation experiments with oats and peas the new material was not much inferior to superphosphate, and superior to basic slag. These results were confirmed by W. Schneidewind and

[1] *Teknish Ugeblad, Christiania*, 1904, **50**, 329; *Chem. Zeit.*, 1904, **28**, 56.
[2] M. Fournier, *Fr. Pat.*, Jan. 1903, 336, 872.
[3] *Fr. Pat.*, Sept. 1903, 335, 509. [4] *Bied. Centr.*, 1904, **33**, 301.

D. Meyer [1] on mustard and oats. While less phosphoric acid was taken up from the Wolter phosphate than from superphosphate, more was taken up than from basic slag. The new material can be kept quite well, and is not hygroscopic.

Mineral phosphates have also been fused in a furnace with lime by W. Mathesius [2] (Berlin), to form a tetrabasic phosphate of calcium. The product is treated with steam under pressure, or with exhaust steam, in a closed vessel, until it crumbles to a dry powder.

Action of Salts on Phosphates.

Salts, such as ammonium salts, which undergo decomposition in the soil, are termed by J. W. Schulow [3] "physiologically acid salts." These, he holds, have the power of rendering phosphates more available by reason of the action of the acid of the ammonium salts upon them. In pot experiments with barley, better results were produced by using a mixture of phosphorite and ammonium salts than by using the two substances separately. This result, however, it may be pointed out, is nothing more than was brought out years before in the Rothamsted experiments and confirmed at Woburn, although the exact explanation of the action may be wanting.

F. K. Cameron and L. A. Hurst,[4] working on the action of water and saline solutions on certain slightly soluble phosphates, state that the phosphates of iron, aluminium, and calcium are all hydrolysed by water, and the solutions always contain free phosphoric acid. Whilst the free acid tends to increase the solubility of the phosphate, the base, although in solution in smaller amount, tends to decrease this solubility. Hence potassium chloride added would decrease the amount of phosphoric acid rendered soluble from phosphates of iron, aluminium, or calcium. The decomposition of the phosphates, either in water or saline solutions, is accelerated by a rise of temperature.

Superphosphate.

The increasing demand, especially abroad, for superphosphate in a finely divided and dry condition has led to the introduction of processes for the artificial drying of superphosphate by heat. A. Grégoire and J. Hendrick [5] experimented on barley with superphosphate that had been dried at 165°, and found that the changes produced in the superphosphate in no way decreased its manurial value.

[1] *Chem. Centr.*, 1904, ii, 788; from *Landw. Jahrb.*, 1904, **33**, 342.
[2] *Eng. Pat.*, June, 1904, 13,361.
[3] *Bied. Centr.*, 1904, **33**, 79.
[4] *J. Amer. Chem. Soc.*, 1904, **26**, 885.
[5] *Chem. Centr.*, 1904, ii, 555.

Potash Salts.

J. Dumont,[1] in investigating the distribution of potash in different soils, found that in one soil, which contained 0·853 per cent. of total potash, potash manures were ineffective, whereas with another, which contained 0·894 per cent. of total potash, they acted very beneficially. A closer examination of the soils, however, showed that in the first case five-sixths of the potash were contained in the finer portions of the soil, but, in the other, seven-tenths of the potash were in the coarse sand. Potash manures, accordingly, may be expected to do good on granitic soils in which, although the amount of potash may be large, it is passive owing to the poverty of the soil in fine material which will readily give up potash.

Experiments have been made by Schneidewind and Ringleben [2] to compare the action of pure potassium salts with that of crude salts in conjunction with lime. When soil was deficient in calcium carbonate, potassium chloride and sulphate were both found to do better than kainite, but where lime was sufficient, kainite was preferable. The action of sodium in presence of potassium is not to be attributed solely to its taking the place of potassium, but, possibly, also to the production of sodium nitrate and phosphate, and to the greater diffusibility of these salts. The chlorine of these manures was found to be distributed chiefly in the straw of cereals and in the leaves of root crops.

Schneidewind and D. Meyer [3] found that sodium chloride, if used with a small amount of potassium, slightly increased the yield of potatoes, but when there was a large amount of potassium the sodium chloride considerably decreased the yield. On the other hand, mangels benefited by the addition in all circumstances. The authors conclude, therefore, that it is better to use the pure potash salts for potatoes, and kainite or other crude potash salts for mangels. It may be pointed out here that the maritime origin of the mangel may have much to do with this result.

T. Schloesing, jun.,[4] shows, by comparison of soil in which maize was grown with the same soil without crop but kept in the same state of humidity, that plants draw the whole of their potassium compounds from the potassium salts dissolved in the water of the soil, and not by direct action of the roots on the solid substances.

[1] *Compt. rend.*, 1904, **138**, 215.
[2] *Landw. Jahrb.*, 1904, **33**, 353; *Abstr.*, 1904, ii, 769.
[3] *Chem. Centr.*, 1904, ii, 788; from *Landw. Jahrb.*, 1904 **33**, 347.
[4] *Compt. rend.*, 1903, **137**, 1206.

Nitrogenous Salts.

Wagner [1] and others found that farmyard manure, when used on garden soil, either alone or with sodium nitrate, gave rise to loss, followed by an increase in the total amount of nitrates, whereas in the case of soil alone, or soil to which sodium nitrate was added, the amount of nitrates remained constant during the whole period of the experiment (64 days). When ammonium salts were used with farmyard manure, a reduction of nitrates occurred for the first twelve days only, then came a considerable increase up to 96 days, after which the nitrates again diminished.

Further experiments by Wagner, also recorded here, on ammonium salts as compared with sodium nitrate, gave, on the average, over a large series of different crops, 43 per cent. of the nitrogen as being utilised by the crop when ammonium sulphate was used, as against 62 per cent. with sodium nitrate.

That nitrogenous salts like ammonium sulphate and sodium nitrate, after being applied for some years, are not devoid of after-effect is shown by the Rothamsted experiments.[2] Barley was grown without manure for two years (1902—1903) on plots on which, for the previous twenty-six years, potatoes, unmanured or variously manured, had been grown. The yield of barley, even in the second year, was twice as high on plots where ammonium salts alone, or sodium nitrate alone, had been previously applied each year as it was on the unmanured plot.

Considerable attention has been directed, especially in France and Belgium, to the occasional occurrence of perchlorates in sodium nitrate. H. Pellet [3] (Paris) read a paper on this subject at the International Congress at Berlin, 1903, in which he called attention to a report of D. Crispo, director of the Antwerp State Laboratory, setting out injurious results due to the use of sodium nitrate containing chlorates and perchlorates. Sodium perchlorate has been found to be more hurtful in its effects than potassium perchlorate, and potassium chlorate is still less harmful. Pellet discusses methods for estimating the amounts of these salts that may be present, and concludes that sodium perchlorate, if present even to the extent of 1 per cent., will be injurious to vegetation, and must not be allowed to occur in commercial sodium nitrate.

[1] *Bied. Centr.*, 1903, **32**, 728.
[2] Rothamsted Experiments, Lawes Agricultural Trust, 1904, p. 22.
[3] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 754.

Utilisation of Sewage.

J. W. Leather[1] has carried out experiments on the utilisation, for the sugar-cane crop, of the effluent derived from the working of the septic tank system at Manjri and Poona (Bombay). Analysis of the sewage was made over a period of six months, and the amounts of the more important plant-foods calculated and compared with the requirements of the sugar-cane during its period of growth. It was found that the sewage contained ample nitrogen and phosphoric acid for the needs of the heaviest crops, although potash, possibly, was somewhat deficient in amount. Drainage experiments on the soil to be used were carried out, a millet (*juar*) crop being grown. As the plants grew, the drainage decreased, and after nine weeks—the sewage being applied as it would be in practice—no drainage whatever occurred. Of the phosphoric acid supplied in the sewage, none whatever was lost in the drainage, and also very little potash, not more than 3 to 4 lb. out of 86 lb. supplied.

Crops.

Food Grains and Fodders.

J. W. Leather[2] has made a very useful and much-needed compilation of the chemical composition of Indian food grains and fodders. All the analyses have been made in India, and, with few exceptions, in the laboratory of the Agricultural Department of the Government of India. The list is a very complete one.

Fruit.

S. U. Pickering[3] in the fourth Report of the Woburn Experimental Fruit Farm deals with the manuring of strawberries, gooseberries, currants, raspberries, and apples. He finds that with strawberries suitable manuring gave, over a period of seven years, an average increase of 12 per cent., and that the use of artificial manures alone gave results only 2 per cent. lower than those with dung. Small dressings were preferable to large, and in no case was it necessary to exceed 12 tons of dung to the acre. Dung gave larger-sized fruit and better quality, and the plants were more healthy. A trial with the application of liquid artificial

[1] *Agricultural Ledger, Calcutta*, 1903, No. 2 (Dictionary of Economic Products, Vol. V, M. 239).

[2] *Ibid.*, No. 7 (Dictionary of Economic Products, Vol. III, F. 669).

[3] *Woburn Experimental Fruit Farm, Fourth Report*, 1904 (Eyre & Spottiswoode).

manures during the swelling of the fruit led to no advantage. In the case of gooseberries, dung produced a darker and more luxuriant foliage, and a formation of larger berries, whereas artificial manures produced stinted bushes with poor yield. Dung also left the soil in better condition, but, as with strawberries, 12 tons to the acre were ample. The experiments with currants and raspberries were not very conclusive, but, as regards apples, there was for the first four years an almost entire absence of effect from manurial treatment, the only exception being in the case of sodium nitrate applied in early or late summer, this occasionally producing a good effect. Pickering holds that analysis of the soil affords but a poor guide to the requirements of fruit trees.

Banana.

J. E. Higgins[1] finds that humus and potash are the principal requirements of the banana crop, and refers to E. W. Hilgard's[2] analysis of the ash of the fruit of the Chinese banana as containing more than 60 per cent. of potash, while the ash of the leaves has $27\frac{1}{2}$ per cent. Lime and phosphoric acid are needed in smaller proportions, as is also nitrogen. The growing of leguminous green crops and the ploughing of them in is recommended.

Sweet Potatoes.

H. H. Cousins[3] has examined different varieties of the sweet potato grown in Jamaica, and finds the total solids to vary from 39·8 per cent. to 30·58 per cent. The highest starch content was 30·94, the lowest 23·74 per cent. The sugars varied from 2·94 per cent. to only 0·232 per cent., and the nitrogen from 0·7 to 0·16 per cent. Rather more than one-fifth of the nitrogen exists as amides. Cousins argues that the low amount of sugar found in many cases is not enough in itself to account for the sweetness of the potato when cooked and eaten, and he has made analyses of samples of the same variety before and after cooking, the results showing that, during the process of cooking, the glucose increased from 0·1 to 4·3 per cent., and the total sugars from 1·6 to 7·69 per cent., the starch being proportionately reduced. Also, on keeping for five weeks, a similar change was found to have occurred, the total sugars increasing from 1·1 per cent. to 4 per cent. during this period.

[1] *Hawaii Agric. Exp. Station*, 1904, *Bulletin* No. 7, "The Banana in Hawaii."
[2] *California Agric. Exp. Station*, 1893.
[3] *Bulletin of Dept. of Agriculture, Jamaica*, Dec. 1904, **2**, (12), 275.

Tobacco.

Manurial experiments with tobacco were carried out by M. Lohmann,[1] and pointed to potassium being chiefly of use for the leaves and roots, phosphoric acid for the stems, and nitrogen equally for all parts of the plant. Excessive manuring is to be avoided, as promoting relatively greater development of stems and roots. Dried blood was found to act favourably as a nitrogenous food. Chlorides and sulphates were considered unsuitable, as decreasing the burning properties of the tobacco. Carbonates, on the other hand, acted favourably.

Tea.

In India, H. H. Mann[2] has continued his researches into the chemistry of tea manufacture, these forming, indeed, the first serious attempt to deal scientifically with this important subject. Mann has shown in his former publications ("The Ferment of the Tea-leaf. Parts I and II") that the fermentation of the tea-leaf during its manufacture is due to the presence of an enzyme of the nature of an oxydase, and that the quantity of enzyme present gives an indication of the quality of the tea that may be produced. He found, further, that during the withering of the leaf the amount of enzyme increased considerably, being sometimes twice as much as that contained in the fresh leaf. This increase went on during the withering process until a maximum point was reached, and then it decreased gradually. Following up this clue, he set about determining more exactly the time at which, under varying conditions of temperature and moisture, the best results were obtained. Another point established was the necessity of conducting the fermentation of the tea-leaf as far as possible under aseptic conditions, and the avoidance of handling of the tea-leaf. The use of antiseptics during the process of fermentation was tried, but chloroform was found to destroy the enzyme, and salicylic acid also slowly did the same. Up to the present no satisfactory antiseptic has been discovered, and reliance has to be placed on the absolute cleanliness of all implements used.

Sugar-Beet.

H. W. Wiley[3] has collected the results of experiments carried out simultaneously at ten experimental stations in the United States for the purpose of showing the influence which environment has on the composition of the sugar-beet.

[1] *Landw. Versuchs-Stat.*, 1904, **58**, 439.

[2] *Indian Tea Association, Calcutta*, 1904, No. 2, "The Ferment of the Tea-leaf. Part III."

[3] *U.S. Dept. of Agric., Bulletin* No. 78.

Milk.

H. D. Richmond [1] gives, from analyses of more than 15,000 samples of milk examined in 1903, the average composition as: total solids, 12·78 per cent.; fat, 3·83 per cent.; solids-not-fat, 8·95 per cent. Richmond further criticises Storch's view as to the fat globules of milk being surrounded by a membrane of mucoid substance, a view in which Storch is supported by M. Beau. Richmond shows that all the observations which Storch has made can be explained without the assumption of the existence of a mucoid membrane, and he gives other experiments which tell against the tenability of such a theory.

B. Sjollema [2] (Groningen), as the result of investigations, comes to the conclusion that the liquid fatty acids of fat in milk do not originate from the cow herself, but are, for the greatest part at least, formed from the butyric acid ferments in the paunch, especially from the readily digestible carbohydrates.

T. S. Dymond [3] in Essex and S. H. Collins [4] in Northumberland have both dealt with variations found in the milk of dairy herds and of individual cows comprising them. They both agree as to the influence of the variations found with individual cows practically disappearing when the mixed milk of a sufficient number forming a herd is taken, and attribute the variations more to the idiosyncracies of individuals than to any regular influence of food, weather, or other conditions. Collins, however, contends that the quality of milk in the north of England is generally inferior to that in the south.

The use of hydrogen peroxide for preserving milk has been introduced by A. Renard,[5] 1·5 per cent. of a 12-volume solution being suggested. If this quantity is added, it is entirely decomposed into water and oxygen in from six to eight hours. Larger quantities decompose much more slowly, and with 5 per cent. added some remains undecomposed even after several days. Milk, although not sterilised by a small quantity of hydrogen peroxide, will, after such treatment, keep much longer than ordinary milk.

Milk in a dry form has now been obtained by boiling milk violently in limited quantity on a heated surface at a temperature rather more than 100°; a cushion of steam is formed between the heated surface and the milk, scorching is thereby prevented, and also

[1] *Analyst*, 1904, **29**, 180.

[2] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 831.

[3] *Report of County Technical Laboratory, Chelmsford*, March 1904, "Variations in the Milk of a Dairy Herd."

[4] *J. Soc. Chem Ind.*, 1904, **23**, 3, "The Composition of Milk in the North of England."

[5] *Mon. Sci.*, 1904, **18**, 39.

the formation of a skin. The heated milk is then drawn in a very fine film on to a heated surface and removed almost at once. This is effected by having two steam-heated cylinders (heated rather above 100° by a pressure of 40 lbs. of steam within them), and the milk is fed continuously between them, so that it is kept violently boiling on these surfaces. It then passes between the two cylinders as they slowly revolve, and is carried on in a thin, uniform film, its water being thus rapidly evaporated. While still apparently moist, it passes a knife edge, and comes off the cylinder in a continuous sheet before it can get discoloured, and on cooling becomes perfectly dry. It can then be taken up with water and used as milk again. The retention of a limited portion of water is necessary, so as to supply water of crystallisation for the milk-sugar and thus prevent changes taking place in this substance.[1]

Bacteria.

Beyerinck[2] confirms Natanssohn's observations as to the presence in sea-water of bacteria that reduce carbon dioxide by oxidation of hydrogen sulphide or thiosulphates. He further obtained a bacterium, *Thiobacillus denitrificans*, which utilises free sulphur, converting carbonates and nitrates into sulphates and liberating carbon dioxide and nitrogen.

Assimilation.

G. L. C. Matthaei[3] has determined the assimilation of carbon dioxide by plants at different temperatures from $-6°$ to 45°, and finds that there is a maximum assimilation specific to each temperature. During assimilation the temperature of the leaf rises.

Germination

A. Wilson[4] maintains that enzymes are not the primary cause of the germination of grain, their appearance being the result rather than the cause. The real starting agents of germination he holds to be the lactic acid bacteria, which, developing acid from the ready-formed sugars during steeping, dissolve the insoluble albumin and liberate the enzymes. He shows that if anything inimical to the bacteria, although harmless to enzymes, be present, germination will not take place.

E. Urbain[5] finds that the origin of the carbon dioxide in ger-

[1] *Ber. V. Inter. Kongress für angewandte Chemie*, Berlin, 1903, **3**, 887.
[2] *Centr. Bakt. Par.*, 1904, **11**, 593.
[3] *Proc. Roy. Soc.*, 1903, **72**, 355.
[4] *J. Amer. Chem. Soc.*, 1904, **26**, 289.
[5] *Compt. rend.*, 1904, **139**, 606.

mination is not the atmospheric air, but that it proceeds from the hydrolysis of proteid matter by the proteolytic enzyme. Nicola Castoro [1] has confirmed the earlier observations of Lawes, Gilbert, and Pugh, and also Boussingault, that in germination no appreciable evolution of free nitrogen takes place.

Attention has been drawn to the impregnation of seed with fertilising materials *before* sowing it, with a view to assisting germination. This has been done at the Woburn Experimental Station (see page 204), and Issleib,[2] of Bielefeld, advocates the use of a mixture of the following salts in equal proportions: ammonium nitrate, potassium nitrate, ammonium phosphate and sodium phosphate, 1 kilogram of the mixture in 5 kilograms of water, the seed to be soaked for 48 hours, then dried and sown. This, it is maintained, will give the first needed stimulus to development and will result in an increase of yield.

Organic Acids in Plants.

E. Charabot and A. Hébert [3] believe the organic acids in plants to be oxidation products of carbohydrates. The acidity due to volatile acids is always highest in the leaves. The combined organic acids increase in amount in the absence of light, and decrease if inflorescence is suppressed

Oxalates were found by W. Benecke [4] to be produced in the maize-plant when grown with sodium nitrate, but not when ammonium salts were used. Amar [5] concluded from his experiments that calcium, supplied as nitrate, was entirely assimilated up to a certain point (varying for each species of plant), and that any excess was eliminated as oxalate, the formation of calcium oxalate being, not, as has been supposed, to eliminate oxalic acid, but rather calcium.

Enzymes.

To Vines [6] we are indebted for setting forth very clearly the present position of our knowledge of the part that enzymes play in proteid digestion, and he has traced out the connection between the proteid digestion in animals and that in plants. The presence of a fibrin-digesting enzyme only occurs in certain plants, and there is no evidence of its independent existence, but there has been discovered a protease of the nature of *erepsin*, which is very generally

[1] *Landw. Versuchs-Stat.*, 1904, **60**, 41.

[2] *Landw. Presse*, No. 84, October, 1904, **31**. "Ein Vorschlag zur Steigerung der Getreideerträge durch Imprägnation des Saatgutes mit Nährsalzen."

[3] *Compt. rend.*, 1904, **138**, 1714.

[4] *Bied. Centr.*, 1904, **33**, 387

[5] *Compt. rend.*, 1903, **137**, 1301.

[6] *Linnean Soc.*, December 1, 1904.

present in plants. Vines,[1] in another contribution, draws attention to the fact that the yeast plant, although a single cell, produces a variety of enzymes or ferments, among these being *diastase*, *invertase*, *zymase*, as well as *protease*, an enzyme which digests proteid matter. The nature of the latter he has investigated more closely and finds it to consist of two *proteases*, the one an *erepsin*, the other probably a *trypsin*.

A. Brachin[2] has found *lactase* to be present in a large number of plants, although absent in certain individuals. Its action is arrested by acetic and oxalic acids, but not by tartaric acid, except in large amount.

B. Abelous and Aloy[3] have found in the juice of potato pulp an oxido-reducing enzyme similar to that in the animal organism, and acting as an oxidising enzyme to some substances, and as a reducing one to others.

In the seeds of several plants has also been found by S. Fokin[4] an enzyme capable of decomposing fats into glycerols and fatty acids. He considers that when the enzyme is truly present there is a quantitative relation between the yield of fatty acids and the amount of seed used.

C. van Iterson, jun.,[5] attributes the power which fungi in general have of attacking cellulose to an enzyme, to which he gives the name *cellulase*.

Starch.

A. Fernbach,[6] by comparing the small, light granules of potato starch with the large, heavy ones, and determining the phosphoric anhydride in each, comes to the conclusion that the small granules consist of a nucleus relatively rich in phosphorus, on which are gradually superposed layers of starch free from phosphorus.

G. Barger[7] has isolated from *Saponaria officinalis* the glucoside *saponaria*, known as "soluble starch." By hydrolysis with mineral acids, glucose is produced and also a substance, *saponaretin*, closely allied to the flavones.

From the valuable record of work issued by Horace Brown[8] from the Guinness Research Laboratory comes a most welcome new method for the rapid estimation of starch in barley and malt.

[1] *Linnean Soc.*, February 4, 1904.
[2] *J. Pharm. Chim.*, 1904, [vi], **20**, 300.
[3] *Compt. rend.*, 1904, **138**, 382.
[4] *Chem. Rev. Fett. Harz.-Ind.*, 1904, **11**, 30.
[5] *Centr. Bakt. Par.*, 1904, **11**, 689.
[6] *Compt. rend.*, 1904, **138**, 428.
[7] *Brit. Assoc. Report*, 1904 (*Chemical News*, 1904, **90**, 183).
[8] *Trans. Guinness Research Lab.*, 1903, 79.

This depends on the fact that when starch is hydrolysed by active diastase under suitable conditions there is a well-defined resting-stage in the action, approximating closely to the equation:

$$\underset{\text{Starch.}}{10C_{12}H_{22}O_{10}} + 8H_2O = \underset{\text{Maltose.}}{8C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{2C_{12}H_{20}O_{10}},$$

100 parts of starch thus yielding 84·4 per cent. of maltose. Hence, if starch of barley or malt be converted by diastase so as to ensure hydrolysis according to the above equation, the determination of the maltose from its cupric-reducing power should give the direct measure of the original starch present. The grain is finely ground, extracted with alcohol, then treated with malt extract, and the starch calculated from the cupric-reducing power of the solution. Three hours' extraction with alcohol is needed for barley and nine for malt. A malt with diastatic power of 80 Lintner should be used. Numerous experiments with the process have given very satisfactory results in comparison with O'Sullivan's method.

The investigations at the Guinness Laboratory have been mainly concerned with the changes which barley undergoes during the early stages of the germinative process. The nitrogenous constituents of barley and malt, especiallv those called the "soluble non-coagulable albuminoids," have been closely studied, the different methods for their estimation examined, and modifications of these have been made or fresh methods devised. Much attention has been given to the estimation of amides and amido-acids, and of tyrosine in presence of mixtures of these.

Further, the estimation of the total amount of nitrogenous substances soluble in water has been worked out for the purpose of getting standard methods for extraction with water; also, the influence of inorganic salts, especially sodium chloride, on the "globulins" has been studied. The second part of the records is concerned with the giving of more definiteness to those "points" which "experts" are accustomed to take into consideration when judging of the "quality" of barley. In this connection the "mealiness" of grain, the changes it undergoes by steeping, and the meaning of "maturity" are specially dealt with. The whole forms a most valuable record of scientific work.

Phosphorus in Foods.

Inquiries by E. B. Hart and W. H. Andrews,[1] as also by A. J. Patten and E. B. Hart,[2] have led to the conclusion that vegetable feeding-stuffs do not contain phosphorus

[1] *Amer. Chem. J.*, 1903, **30**, 470.

[2] *New York Agr. Expt. Station Bulletin*, 1904, No. 250.

to any appreciable extent in inorganic combination; germinating grains, they find, are rich in organic phosphorus, and this is not transformed into organic forms during germination. It is suggested in the case of wheat-bran that the soluble phosphates exist in the form of a magnesium-calcium-potassium salt of a phospho-organic acid. Phosphorus in organic combination has similarly been found by Weirich and Ortlieb [1] in wines.

Nitrogen in Wheat.

E. Fleurent [2] finds that the relation of gluten to total nitrogen in the case of different varieties of wheat frequently varies, and that the gluten must be determined separately and not be taken simply from the estimation of total nitrogen.

Arsenic in Farm Crops.

Field experiments [3] conducted on cereal and root crops with superphosphate free from arsenic, and with superphosphate containing arsenic, or to which arsenic in varying proportions was added, showed that the use of artificial manures was not a cause of the contamination of barley (to be used in brewing) with arsenic. In no case was arsenic found in the ripe barley grain, or in the bulbs of the roots. Very small quantities were, however, detected in the straw of the cereals and the leaves of the root crops.

J. Augustus Voelcker.

[1] *Chem. Zeit.* 1904, **28**, 153. *Compt. rend.*, 1903, **137**, 1313.
[3] Report of the Royal Commission on Arsenical Poisoning, 1904.

MINERALOGICAL CHEMISTRY.

Advances in mineralogical chemistry consist for the most part of contributions to our knowledge of the composition of minerals, in the shape of analyses scattered in short papers through the pages of many periodicals. Work resulting either in the discovery of new principles or in the co-ordination of established facts is only of rare appearance. A report on the progress of this branch of science must therefore, from the necessities of the case, partake somewhat of the nature of a catalogue, and the compiler, in marshalling his material, has first to settle whether to aim at completeness, or, failing this, has only to decide on a standard by which to try the importance of the facts claiming admission to his chronicle.

The second course, in spite of the disadvantages attendant on the introduction of a large personal equation, is the one which will be adopted by the present writer. In the following pages an attempt will be made to give a brief outline of progress in what may be termed the general and physical chemistry of minerals, and to this will succeed a list of analyses, important because throwing light on the chemical formula of the material analysed, or noteworthy on account of the rarity or peculiar properties of the mineral examined.

General and Physical Chemistry of Minerals.

With the advance of physical chemistry, attempts have naturally been made to apply the principles derived from the study of aqueous solutions and mixed crystals to the elucidation of problems in mineralogy and petrology.

Research of this kind, which has so far been chiefly directed to the investigation of salt deposits and of crystalline igneous rocks, has led during the year to important results in each of these fields.

Salt Deposits.—To van't Hoff and his pupils[1] we owe five more, Nos. xxxiv—xxxviii, of those "Investigations into the Conditions of

[1] *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 518, 576, 659, 935, 984; *Abstr.*, 1904, ii, 417, 492, 561, 570.

A useful summary of van't Hoff's earlier work on this subject has been published by E. F. Armstrong, *Brit. Assoc. Report*, 1901, 262.

Formation of Oceanic Salt Deposits," which have now practically solved the complex problem of the Stassfurt beds.

Of these memoirs, xxxiv and xxxv give an account of the study of the maximal tension and composition of the constant solutions at 83°. The salts the mutual relations of which are considered are: bischofite ($MgCl_2,6H_2O$), carnallite ($KCl,MgCl_2,6H_2O$), glaserite ($3K_2SO_4,Na_2SO_4$), kainite ($KCl,MgSO_4,3H_2O$), kieserite ($MgSO_4,H_2O$), langbeinite ($K_2SO_4,2MgSO_4$), loeweite ($Na_2SO_4,MgSO_4,2\frac{1}{2}H_2O$), thenardite ($Na_2SO_4$), and vanthoffite ($3Na_2SO_4,MgSO_4$). The results are tabulated and represented graphically.

Number xxxvi, an especially important paper, gives a review of previous results and traces the conditions under which combinations of minerals separate from solutions at temperatures between 25° and 83°. The preparation of the two salts $K_2Ca_5(SO_4)_6$ and

$$2K_2O,2MgO,11B_2O_3,20H_2O$$

is described in number xxxvii, and the identity of the minerals mamanite and polyhalite is established in number xxxviii. In this connection, it is of interest to note that C. Przibylla[1] finds that the sum of the molecular volumes of sylvite (KCl) and bischofite

$$(MgCl_2,6H_2O)$$

is 165·39, while the molecular volume of carnallite ($KCl,MgCl_2,6H_2O$) is 173·57. The application of pressure to carnallite will therefore tend to produce sylvite and bischofite, thus suggesting an explanation of the occurrence of the latter salt in veins of crushed carnallite.

Dolomitisation.—An important contribution to this subject has been made in the publication by the Royal Society of the results of a chemical and microscopical examination of the core obtained from the bore-hole put down in the Atoll of Funafuti.

Under the direction of Prof. J. W. Judd, no fewer than 133 analyses were made of material from the main core. The results show that the rock is almost entirely composed of the carbonates of calcium and magnesium. The amount of calcium phosphate present is very small, 0·124 to 0·288 per cent., and the quantity of insoluble matter almost negligible, 0·001 to 0·083 per cent. Organic matter occurs in the upper part of the core, but below 50 feet the quantity present is inappreciable.

In the upper part of the reef the proportion of magnesium carbonate increases from the top downwards till maxima of about 16 per cent. are reached at depths of 16 and 25 feet respectively, with a minimum of 12 per cent. between. Below 25 feet, the quantity of magnesium carbonate decreases, and from 50 feet down to 637 feet does not exceed 5 per cent. From 637 feet to 658 feet, the proportion of magnesium carbonate rapidly increases to 40 per cent., a value which is maintained

[1] *Centr. Min.*, 1904, 234; *Abstr.* 1904, ii, 416.

with slight variations to the bottom of the core (1114½ feet). The percentage (45·65) required to form dolomite is never quite reached, the nearest approach being 43 per cent. at 950 feet.

A microscopical examination made by C. G. Cullis has established the interesting fact that aragonite crystals are only met with in the upper parts of the core, dolomite crystals only in the lower.

In the discussion of the bearing of these observations on theories of dolomitisation, it is pointed out that the quantity of magnesium carbonate secreted by organisms in forming their skeletons does not seem to exceed 1 per cent. of the total weight, but that after the death of the organism the proportion of magnesium carbonate may be increased by the leaching out of calcium carbonate. This view is in harmony with what is known as to the solubility of the carbonates of calcium and magnesium, and the presence of the latter in the upper part of the reef may be attributed to such a process. The great increase in the amount of magnesium carbonate in the lower part of the core, below 637 feet, is probably due to some other cause, possibly to an interchange of bases with the sea-water, and it seems likely that an attack on this problem by the aid of the methods developed by van't Hoff may lead to important results.

Uralitisation.—L. Duparc and T. Hornung[1] have studied this phenomenon by means of a series of rocks from the Northern Urals, which show all stages in the passage from pyroxene to green amphibole. The analyses, I. pyroxene, II. amphibole, of these minerals separated from the rocks are inconsistent with the view that the process of uralitisation is one of molecular transformation. Moreover, as the rocks are perfectly fresh, the phenomenon cannot be explained as due to hydrochemical alteration. The authors therefore suggest that after the pyroxene had crystallised out it was acted on by the residual magma and converted in patches into amphibole.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Loss on ignition.	Total.
I.	50·91	2·64	—	10·07	23·33	13·30	—	—	—	100·25
II.	43·34	12·60	10·44	7·92	13·06	12·60	0·02	1·90	0·22	102·10

Silicates.—The study of the compounds which crystallise out when molten mixtures of silicates are cooled has long been a favourite one with mineralogical chemists, and, thanks to the researches of the French school, methods for the preparation in the laboratory of crystals of many of the most important rock-forming minerals have been known for a number of years. Research of this kind has of late received a special stimulus, partly due to the growing conviction that the crystallisation of silicates from molten magmas must follow laws similar to those which the advance of physical chemistry has shown

[1] *Compt. rend.*, 1904, **139**, 223; *Abstr.*, 1904, ii, 621.

to hold in the case of alloys, and of salts separating from solutions, and partly owing to the influence of Meyerhoffer,[1] who has emphasised the importance of the eutectic point as conditioning the course of crystallisation. Among the most active workers in this field have been J. H. L. Vogt and C. Doelter, the latter associated with a number of pupils. The recent contributions of both these investigators deserve more than a passing consideration.

At the close of 1903, Vogt[2] published the first part of a work entitled *Die Silikatschmelzlösungen*, in which he sums up the results of researches conducted by him during the past twenty years. Incorporated with the earlier matter are many new observations, and the book sets forth a number of conclusions which are based partly on facts already published, and partly on determinations of melting points, &c., which are to be given in detail in the second portion, which has not yet appeared. Vogt's observations have been made for the most part on furnace slags, and are chiefly concerned with ortho- and meta-silicates belonging to the olivine and pyroxene groups. He has also examined a number of products obtained by R. Åkerman, who fused together the constituents of certain silicates. These molten masses were in all cases quickly cooled under ordinary conditions of pressure. Water, carbon dioxide, and fluorine, which play so large a part in the production of many rock-forming minerals, were excluded.

The slags most exhaustively studied were composed of silicates of calcium, magnesium, and iron. In such substances, a number of well-defined minerals may be detected, as, for instance, olivine, enstatite, augite, wollastonite, gehlenite, &c. In order to compare the composition of the various slags, the following graphical method was employed: it was assumed that in the metasilicates magnesium and iron replace one another in all proportions, and the ratios (Mg,Fe)O : CaO were plotted as abscissæ, while the "degrees of acidity" were plotted as ordinates, the degree of acidity being defined as the ratio, oxygen combined with acid : oxygen combined with base. Thus for a typical orthosilicate, $2R_2O,SiO_2$, the degree of acidity = 1, while for a metasilicate, R_2O,SiO_2, the degree of acidity = 2. It will be seen that the compositions of a number of slags, &c., can in this way be represented by points on a diagram. The mineralogical character of the crystals corresponding with each point was then carefully determined, and on examining the diagram it was found that it broke up naturally into well-defined mineralogical fields. In other words, it became evident that a particular mineral only crystallised out when the slag had a composition varying between fairly well-defined limits. On over-

[1] *Zeit. Kryst. Min.*, 1902, **36**, 593.

[2] Die Silikatschmelzlösungen. Von J. H. L. Vogt. 1903. Christiania. pp. v and 161. See also *Centr. Min.*, 1904, 49.

stepping these limits, another mineral took its place. To the exact delimitation of the field proper to each mineral, Vogt has devoted an immense amount of study. The results are set forth in a striking coloured diagram, constructed on the principles described above from a large number of analyses, and are fully discussed in the text, which also deals with silicates containing manganese.

As specimens of the facts observed, we may cite the following: the limit between true olivine and augite is reached when the fused mass has a degree of acidity represented by 1·6. Again, oblique pyroxenes and calcium metasilicates (occurring either as wollastonite or as hexagonal crystals) crystallise from magmas the acidity of which ranges between 1·65 and 2·50; if the ratio Ca : Mg in the magma is greater than 7 : 3, calcium metasilicate separates; if it is less, an oblique pyroxene is the result. Slags containing calcium and aluminium were also investigated in the same way, and a similar diagram constructed. In this connection, Vogt devoted special attention to the series of minerals known as melilites. He has shown that they are to be regarded as mixed crystals composed of gehlenite, $R_3^{II}Al_2Si_2O_{10}$ and Åkermanite, $R_4Si_3O_{10}$, where R = Ca, Mg, Fe, &c. The latter substance has not been found as a mineral, but Vogt has succeeded in preparing it in tetragonal crystals having the composition $(Ca,Mg)_4Si_3O_{10}$.

These observations, many of which were made as far back as 1884, led Vogt to the general conclusion that the nature of the minerals which crystallise from a molten mass depends essentially on the chemical composition of that mass. The minerals are, in fact, products of the chemical affinities of the predominant constituents, and mass action plays a decisive part in their formation. Moderate changes in the physical conditions under which they are produced, such as the temperature to which the mass has been heated, the rate at which it is cooled, the pressure under which it crystallises, either exert no influence at all, or modify but slightly the course of crystallisation.

As the outcome of his later work, he now lays down the proposition that the boundaries between the various fields on the diagram described above indicate the composition of the eutectic mixtures of the minerals concerned. Again, from the study of the order of crystallisation deduced from microscopic examination of thin sections of slags, he finds that the mineral which is in excess as regards the eutectic point comes out first, although the phenomena are sometimes complicated by effects due to supersaturation. If the melting points of two minerals are nearly the same, the eutectic mixture consists of about equal proportions of the two constituents; if, on the other hand, the melting points are very different, the eutectic contains an excess of that constituent which has the lowest melting point. The melting

point of the eutectic may lie from 200° to 400° below that of the most fusible constituent. The proportions of the components of some of the eutectic mixtures he has investigated are as follows: diopside 45 per cent. and calcium metasilicate 55 per cent.; augite 70 per cent. and olivine 30 per cent.; orthoclase 74¾ per cent. and quartz 25¼ per cent.

Further, he comes to the conclusion that silicates are but slightly dissociated on fusion, and that we may apply to their mutual solutions the van't Hoff formula for finding the depression of the freezing point, $t = \frac{m}{M} \cdot \frac{0{\cdot}02T^2}{\lambda}$ (where m is the weight of solute in 100 grams of solvent, M the molecular weight of the solute, T the melting point of the solvent in absolute temperature, λ its latent heat of fusion).

Working on these lines, he finds that the formula $CaMgSi_2O_6$ must be assigned to diopside when in solution, whilst olivine is represented by the simple formula Mg_2SiO_4, and the anorthite molecule by $CaAl_2Si_2O_8$.

These important conclusions are largely based on the results of pyrometric measurements as yet unpublished.[1]

Vogt has also attempted to classify the series of mixed crystals met with among the silicates by means of the principles established by Bakhuis-Roozeboom in his work on the solidification points of mixed crystals of two substances. He adduces evidence to show that the olivine and augite series may both be assigned to type I of the scheme drawn up by Bakhuis-Roozeboom, and discusses the position of the melilite series and of the plagioclase felspars without arriving at any very definite results.

He concludes by expressing his conviction that it is in this direction we must seek the path to be followed in future investigation.

While Vogt has attempted to apply the principles of physical chemistry to the study of silicates, C. Doelter and his pupils[2] feel that the time is hardly ripe for such an enterprise, and find themselves compelled to traverse some of Vogt's conclusions.

On the experimental side, Doelter has determined (1) the melting points of a number of silicates, (2) the melting points of mixtures of two silicates taken in various proportions, (3) the melting points of the glasses obtained when molten mixtures are quickly cooled. He has also studied the products which crystallise from the fused masses, and has determined the limits of temperature between which they separate and the order of their appearance.

[1] The second part of Vogt's work appeared as these pages were in the press.

[2] C. Doelter, *Sitzungsber. K. Akad. Wiss. Wien.*, 1904, **113**, i, 177. M. Vučnik, *Centr. Min.*, 1904, 295, 340, 364; B. Vukits, *Centr. Min.*, 1904, 705, 739.

In determining melting points, Doelter makes use of electric resistance furnaces of various types, and measures the temperature by means of a rhodium-platinum thermo-couple. The following are some of the values obtained : anorthite, 1230° ; labradorite, 1210° ; albite, 1150—1160° ; orthoclase, 1210° ; adularia, 1215° ; diopside, 1255° ; augite, 1185° ; olivine, 1280° ; leucite, 1310° ; magnetite, 1250° ; achmite, 965°. It will be noticed that the melting points of these important minerals lie within a comparatively narrow range of temperature. On making mixtures, in various proportions, of pairs of these minerals, it was found that the melting point of the mixture lies between the melting points of the components and often approximates to the arithmetic mean of these. Here there is no indication either of lowering of the melting point or of the existence of a eutectic mixture.

On the other hand, the glasses obtained on rapidly cooling the molten masses fuse, as a rule, at temperatures below the melting points of the most fusible of their constituents.

In order to study the order of crystallisation, Doelter employed a very small electric resistance furnace, which could be placed on the stage of a polarising microscope. The silicates to be examined were supported in the furnace on dishes made of quartz glass. By the aid of this ingenious device, Doelter has shown that a number of the most important rock-forming minerals separate at temperatures which lie between 1180° and 930°. He has, moreover, been enabled to study the effects of supersaturation, and to observe the formation of new substances resulting from chemical action taking place between the two silicates when melted together.

The general conclusions to which these researches have led him are as follows : when two minerals are fused together and allowed to cool, we may meet with the following phenomena.

(1) The two minerals separate out again.

In this case, we may find (*a*) that the mineral present in largest quantity comes out first. Here the eutectic point is of importance ; (*b*) that the two minerals separate alternately or simultaneously. This phenomenon, which is a common one, is due to superfusion. The order of crystallisation may often be reversed by introducing a crystal of one or other of the components ; (*c*) that the less plentiful constituent crystallises first. This is to be attributed to the comparative insolubility of the compound and is often observed.

(2) New compounds separate in addition to the original ones, or one of the compounds changes into another.

(3) Only one mineral separates. In this case, the second constituent either remains in the form of glass or is taken up by the other,

anomalous mixed crystals being formed. This case is but rarely met with.

Further, he believes that the molten silicates are highly dissociated and contain molecules of oxides, FeO, MgO, &c., as well as molecular groupings, such as $KAlSi_2O_6$ and $KAlSi_3O_8$. On cooling, simple oxides and aluminates separate out first, followed by the simpler silicates, and then by the more complex ones. It will be observed that many of Doelter's results appear to be incompatible with the views advanced by Vogt, and this is more especially the case with those obtained from experiments made to test the validity of the van't Hoff formula when applied to the calculation of the molecular weights of silicates. These experiments gave such discordant values, even in the simplest cases examined, that Doelter concludes that we are not justified in applying the formula to mixtures of molten silicates. He points out, moreover, that we should hardly expect it to yield results in the case of solutions which are in many instances highly concentrated and probably often much dissociated.

New Minerals.

The following new minerals are of interest.

Astrolite, described by R. Reinisch,[1] is found as small, greenish-yellow spheres imbedded in a black carbonaceous rock which occurs in a diabase-tuff at Neumark in Saxon Vogtland. The optical characters suggest orthorhombic symmetry, and from an analysis the metasilicate formula $(Al,Fe)_2Fe(Na,K)_2(SiO_3)_5,H_2O$ has been deduced.

Coronadite is an opaque mineral not unlike psilomelane in appearance. It occurs in the Clifton-Morenci district, Arizona, and has been described by Lingren and Hillebrand.[2] Analysis of material not quite free from impurity led to the formula $R''Mn_3O_7$, where R″ stands for Pb and Mn, the former predominating. Small quantities of Cu, Zn, and Fe are also present.

Cryolithionite, described by N. V. Ussing,[3] is a well-defined mineral, occurring in large, colourless, rhombic dodecahedra in the cryolite of Ivigtut, Greenland. Analysis of pure material established the formula $Li_3Na_3Al_2F_{12}$. This substance is interesting as containing the highest percentage of lithium of any mineral yet known. Although it has certain points in common with cryolite, it is crystallographically more closely related to the garnet and sodalite groups.

Erikite has been described by O. B. Böggild[4] from the nephelite-syenite

[1] *Centr. Min.*, 1904, 108; *Abstr.*, 1904, ii, 268.

[2] *Amer. J. Sci.*, 1904, **18**, 448.

[3] *Overs. K. Danske Videnskab. Selsk. Forhandl.*, 1904, 3; *Abstr.* 1904, ii, 347.

[4] *Meddel. om Grönland*, 1904, **26**, 93; *Abstr.*, 1904, ii, 49.

at the Tunugliarfik-Fjord, Greenland. The brown, well-developed crystals are orthorhombic. On microscopic examination of a thin section, the mineral is seen to consist of an intergrowth of two substances, of which the predominant one (erikite) is yellow, strongly refracting and birefringent, while the other, of which the refraction and birefringence are weak, is probably hydronephelite. An analysis of the mixture gave the following result:

SiO_2.	P_2O_5.	$(Ce,La,Di_2)_3O_3$.	ThO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
15·12	17·78	40·51	3·26	9·28	1·81	5·63	6·28	99·67

Erikite is placed in a group comprising compounds of silicates, titanates &c., with columbates, tantalates, phosphates, antimonates, &c. In the cubic members of this group (pyrochlore, lewisite, &c.), the ratio of the acid oxides $RO_2 : R_2O_5$ is $=$ or < 1, whilst in all the others it is $=$ or > 2.

Morencite is the name given by Lingren and Hillebrand[1] to a fibrous, optically well individualised mineral observed by them from the Clifton-Morenci district, Arizona. It consists chiefly of silica and ferric oxide with small quantities of MgO, CaO, and FeO.

Nuegite is a tetragonal mineral described by Tsunashiro Wada[2] from Naëgi, near Takayama, province of Mino. An analysis by T. Tamura gave the following results:

SiO_2.	UO_2.	ThO_2.	Ta_2O_5.	Nb_2O_5.	CeO_2.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
34·89	28·27	16·50	7·00	4·10	1·59	1·60	1·71	0·57	3·12	99·35

Palmerite is a white, amorphous mineral resembling kaolin in appearance. It occurs in a guano deposit near Controne, Salerno, Italy, and has been described by E. Casoria.[3] Its formula is

$$HK_2Al_2(PO_4)_3,7H_2O.$$

Radiotine.—R. Brauns[4] has described the small spheres of this fibrous mineral which occur in serpentine in the upper devonian picrite of the neighbourhood of Dillenburg. Analysis showed the composition to be the same as that of serpentine, $Mg_3Si_2O_7,2H_2O$, but it has a lower specific gravity and is not attacked by hydrochloric acid.

Teallite.—This interesting Bolivian mineral occurs in thin graphite-like folia which have been determined by Prior[5] to be probably orthorhombic. The analytical results agree very closely with those required

[1] *Amer. J. Sci.*, 1904, **18**, 455.

[2] *Minerals of Japan*, Tōkyō, 1904. This work contains many analyses of Japanese minerals.

[3] *Atti Accad. Georgofilé*, 1904, [v], 1.

[4] *Jahrb. Min.*, 1904; *Beil.-Bd.*, **18**, 285; *Abstr.*, 1904, ii, 350.

[5] *Min. Mag.*, 1904, **14**, 21; *Abstr.*, 1904, ii, 743.

for the simple formula $PbSnS_2$. It exhibits relations to franckeite and cylindrite.

Thorianite.—This mineral, first obtained by W. D. Holland, has been discovered by A. K. Coomára-Swámy in the bed of a stream near Kondurugala, Ceylon, where it occurs in heavy, black, water-worn cubic crystals associated with zircon, ilmenite, and small quantities of another mineral, probably thorite. A very small amount has also been discovered by Coomára-Swámy in a pegmatite vein on the Ambalawa estate, Gampola. Analyses made in the laboratory of the Imperial Institute under the direction of Prof. W. R. Dunstan[1] gave the following results:

ThO_2.	CeO_2.	$(La,Di)_2O_3$.	ZrO_2.	UO_3.	Fe_2O_3.	PbO.	SiO_2.	Insol.	Total.
72·24	6·39	0·51	3·68	11·19	1·92	2·25	1·34	0·41	99·93
76·22	8·04		trace	12·33	0·35	2·87	0·12	—	99·93

Sir W. Ramsay[2] has also investigated this mineral and finds it to contain helium.

Mineral Analyses.—During the year, fresh investigations of the chemical composition of a number of minerals have been made. In some cases, the work has led to the confirmation or revision of doubtful formulæ, while in others it has been undertaken in the hope of detecting rare elements.

Examination of Minerals for Radioactivity.—Owing to the interest aroused by radium, a number of workers have determined the effect produced by various minerals on photographic plates and in discharging electroscopes. Thus M. G. Bardet,[3] using the photographic method, concludes that with rare exceptions all active minerals contain uranium, while B. B. Boltwood[4] finds that the effect produced on an electroscope is proportional to the percentage of uranium present. J. Hoffmann[5] has examined the uranium minerals from Schlaggenwald and finds that torbernite, autunite, zippeite, and pitchblende rapidly affect a photographic plate, whilst the action of uranocher, uranotile, and gummite is less intense. Kolbeck and Uhlich,[6] working on similar lines, find that pitchblende from Johanngeorgenstadt gives the best result. S. M. Losanitsch[7] has detected radioactivity in the cinnabar from Avala and Bare, in Servia, and from Idria in Austria. He attributes the photographic action, which is weaker than that of

[1] *Nature*, 1904, **69**, 510.
[2] *Ibid.*, 533, 559; *Abstr.*, 1904, ii, 745.
[3] *Bull. Soc. franç. Min.*, 1904, **27**, 63.
[4] *Amer. J. Sci.*, 1904, **18**, 97; *Abstr.*, 1904, ii, 666.
[5] *Zeit. prakt. Geol.*, 1904, **12**, 123, 172.
[6] *Centr. Min.*, 1904, 206.
[7] *Ber.*, 1904, **37**, 2904; *Abstr.*, 1904, ii, 743.

pitchblende, to the presence of radioactive mercury, and points out that the barytes which accompanies the cinnabar is inactive.

D. Mawson and T. H. Laby,[1] who have examined some Australian minerals, find that only those which contain thorium and uranium exhibit a high degree of activity. H. N. McCoy[2] has observed the effect on an electroscope produced by twelve specimens of uranium minerals, including pitchblende, gummite, and carnotite, chiefly from American sources. He concludes, like Boltwood, that the activity is directly proportional to the amount of uranium in the ore. On comparing the ores with pure uranium compounds, he found that the former were proportionately more active than the latter in the ratio of 5·7 : 1. He believes that his experiments support the theory that radium is a decomposition product of uranium. M. F. Pisani[3] has examined by the photographic method a very large number of minerals of all kinds. He finds that with but few exceptions, including certain fluorides, all radioactive minerals contain uranium or thorium or both. Among the substances which had the strongest effect, he notes thorite, orangite, euxenite, aeschynite, trogerite, zeunerite, mixite, turnerite, uranocircite, uranite, monazite, pitchblende, cleveite, and violet fluorspar (from Cumberland). C. Winkler,[4] in the course of an interesting discussion entitled "Radioactivität und Materie," points out that, in spite of the chemical resemblance between radium and barium, we do not find radioactive barytes accompanying radium ores, the property being apparently entirely dependent on the presence of uranium. We must, however, notice in this connection that R. Nasini[5] claims to have detected radioactivity in the barytes prepared from the Albano deposits.

Presence of Rare Elements in Certain Minerals.

Germanium is known to exist in franckeite (0·1 per cent.), in canfieldite (1·82 per cent.), in an iron-black mineral from Bolivia (4·99 per cent.), and in argyrodite (6·42 per cent.). It has also been reported by Krüss in euxenite (0·1 per cent.) and by Chrustschoff in samarskite (1·5 per cent.). The work of these two authors has, however, been recently revised by G. Lincio,[6] who, after very careful examination, has been unable to detect the element either in samarskite from the Urals and from Mitchell City, or in euxenite from Kragero and Spangereid. He concludes that sulpho-salts afford at present the only known sources of germanium.

[1] *Proc. Roy. Soc. New South Wales*, 1904, 37.
[2] *Ber.*, 1904, **37**, 2641.
[3] *Bull. Soc. franç. Min.*, 1904, **27**, 58 ; *Abstr.*, 1904, ii, 530.
[4] *Ber.*, 1904, **37**, 1655 ; *Abstr.*, 1904, ii, 462.
[5] *Atti R. Accad. Lincei*, 1904, **13**, i, 367 ; *Abstr.*, 1904, ii, 461.
[6] *Centr. Min.*, 1904, 142 ; *Abstr.*, 1904, ii, 348.

Indium and *gallium* have been detected with the spectroscope by Rimatori [1] in blendes from Sardinia. The percentage of indium was estimated in a specimen from Riu Planu Castangias, weighing eighty grams, and the high value 0·12 per cent. obtained. These blendes were also found to contain up to 0·79 per cent. of cadmium.

Yttrium and *ytterbium* have been shown by W. J. Humphreys [2] to be present in most specimens of fluorspar. The remarkable sensitiveness to heat of fluorspar from Amelia Court House, Virginia, led to this investigation; it becomes luminous when merely held in the hand for a few minutes. On finding that the arc spectrum of this fluorspar showed the presence of yttrium and ytterbium, more than a hundred others were examined. The specimens richest in the two elements proved to be those from Amelia Court House, Corocoro, Bolivia, and Llano County, Texas. The two latter resembled the former in their sensitiveness to heat. Of the English specimens examined, those from Cumberland, Durham, and Northumberland showed a fair amount of yttrium, those from Cornwall and Devon but little.

Special Reactions of Minerals.

Calcite and Aragonite.—In 1901, Meigen pointed out that aragonite and calcite could be readily distinguished by the colours of the products obtained when the powdered minerals were boiled with aqueous solutions of cobalt nitrate. This discovery aroused considerable interest at the time, and it was generally admitted that the differences in colour were probably due to the formation of basic cobalt carbonates differing in composition. That this is actually the case has now been shown by A. Lange,[3] a pupil of Meigen's, who has examined the composition of the substances produced under varying conditions of concentration. He concludes that the lilac-coloured compound made by boiling aragonite with concentrated solutions of cobalt nitrate is $2CoCO_3,3Co(OH)_2,H_2O$. The blue compound obtained from calcite under similar conditions is probably $CoCO_3,3Co(OH)_2$. If dilute solutions are employed, the product from aragonite is $CoCO_3,2Co(OH)_2$, and calcite, if very finely divided, yields a substance of the same composition and colour. He finds, moreover, that the products obtained from aragonite are less liable to oxidation than those given by calcite. If cobalt chloride is used instead of the nitrate, the results are on the whole similar to those quoted, but if the sulphate is employed, so much of it becomes included in the product that no satisfactory quantitative estimations can be made.

[1] *Atti R. Accad. Lincei*, 1904, **13**, i, 277.
[2] *Astrophysical Journal*, 1904, **20**, 266.
[3] *Inaug. Diss. Freiburg i. Br.*, 1904.

Calcite and Dolomite.—F. Hinden [1] has proposed the following tests for distinguishing between these substances. (A) The powdered mineral is shaken with cold 10 per cent. solution of ferric chloride. If calcite is present, carbon dioxide is evolved and a brown precipitate produced Dolomite undergoes no change. The test may be made roughly quantitative by taking 1 gram of mineral and adding 5 c.c. of a 5 per cent. solution of potassium thiocyanate. A cold solution of 10 per cent. ferric chloride is then to be added, until after shaking a permanent red colour remains. Under these conditions, 1 c.c. of ferric chloride corresponds with about 8 per cent. of calcite present. (B) Calcite boiled with a 10 per cent. solution of copper sulphate gives a blue basic carbonate of copper, while dolomite remains unchanged.

Quartz.—F. Rinne [2] calls attention to the solvent action exerted on finely divided quartz by caustic alkalis and alkaline carbonates at 100° and by water at 300°, and points out the application of this in the production of so-called "Kalksandsteine," of which there is a large annual output in Germany. In this process, bricks are made from quartz-sand and slaked lime and heated for ten hours in a boiler at 174°. The particles of sand are then found to be firmly held together by a cement formed by the action of the lime and silica, the result being really a "silicate sandstone." From a microscopical examination, Rinne concludes that the cement is of a zeolitic nature, and that the excess of lime becomes converted into calcite.

Mineral Analyses.

Amblygonite.—A pure specimen from a large deposit of the massive white mineral at Pala, San Diego Co., California, analysed by W. T. Schaller,[3] gave the following results:

P_2O_5.	Al_2O_3.	Fe_2O_3.	MnO.	MgO.	Li_2O.	Na_2O.	H_2O.	F.
48·83	33·70	0·12	0·09	0·31	9·88	0·14	5·95	2·29

Antigorite.—Two specimens of this variety of serpentine have been described by A. Hamberg [4] from Persberg and the Ko mine at Nordmarken respectively. Analyses by Elsa Cronqvist agree well with the formula $H_4Mg_3Si_2O_9$, part of the MgO being replaced by FeO.

Beryl.—The composition of beryl has been studied by J. H. Pollok,[5] who finds that the beryllium oxide prepared from Limoges beryl can be separated into fractions having different equivalents either by precipitation with ammonium carbonate, by crystallisation of the sulphate,

[1] *Verh. nat. Ges. Basel*, 1904, **15**, 201. [2] *Centr. Min.*, 1904, 333.
[3] *Amer. J. Sci.*, 1904, **17**, 191; *Abstr.*, 1904, ii, 348.
[4] *Geol. Fören i Stockholm Förhandl.*, 1904, **26**, 67; *Abstr.*, 1904, ii, 745.
[5] *Trans.*, 1904, **85**, 1630.

or by distillation of the chloride. He concludes that the mineral from Limoges contains at least one new element in addition to beryllium.

Boothite.—A massive specimen of this rare form of copper sulphate from Pala, San Diego Co., California, was found by W. T. Schaller [1] to be well represented by the formula $CuSO_4,H_2O,6H_2O$.

Clandetite.—A specimen of this monoclinic variety of arsenious oxide from Szomolnok, Hungary, has been analysed by J. Loczka,[2] who found in it 75·99 per cent. of arsenic; the formula As_2O_3 requires 75·78 per cent. The crystallography of the mineral from this locality has been fully determined by Schmidt.

Cylindrite.—Two specimens from Poopó, Bolivia, have been examined by G. T. Prior.[3] Up to the present, the composition of this mineral has rested on an analysis by Frenzel. Prior's results lead him to regard cylindrite as a definite mineral species of the probable formula $3PbSnS_2 + SnFeSb_2S_8$.

Pb.	Fe.	Ag.	Sn.	Sb.	S.
35·24	2·81	0·50	25·65	12·31	23·83
34·58	2·77	0·28	25·10	12·98	23·88

Cyrtolite.—A specimen of the altered zircon from Bedford, N.Y., examined by L. McI. Luquer,[4] contained 53·56ZrO_2, 27·24SiO_2, and 4·35U_3O_8. The latter is due to inclusions of uraninite.

Emmonsite.—A green substance occurring in mammillary forms at Cripple Creek, California, has been identified with this rare mineral by W. F. Hillebrand.[5] The analysis quoted below does not lead to any satisfactory formula.

TeO_2.	Fe_2O_3.	P_2O_5.	Al_2O_3.	SiO_2.	H_2O at 100°.	H_2O >100°.
70·71	22·76	0·34	0·56	0·88	0·21	4·54

Franckeite.—In connection with his work on teallite and cylindrite (*q. v.*), Prior has analysed two specimens of franckeite, I. from Poopó, II. from the Trinacria mine near Poopó. A consideration of the results of these analyses, and of the values previously obtained by Winkler, leads him to suggest $3PbSnS_2 + Pb_2FeSb_2S_8$ as a probable formula for the species.

	Pb.	Fe.	Zn.	Ag.	Sn.	Sb.	S.
I.	46·23	2·69	0·57	0·97	17·05	11·56	21·12
II.	48·02	2·74	—	0·99	13·89	13·06	20·82

Gadolinite.—G. P. Tschernik [6] has analysed material from Idaho and Ytterbia.

[1] *Amer. J. Sci.*, 1904, **17**, 192; *Abstr.*, 1904, ii, 348.
[2] *Zeit. Kryst. Min.*, 1904, **39**, 520; *Abstr.*, 1904, ii, 666.
[3] *Min. Mag.*, 1904, **14**, 21; *Abstr.*, 1904, ii, 743.
[4] *American Geologist*, 1904, **33**, 17.
[5] *Amer. J. Sci.*, 1904, **18**, 433.
[6] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 287; *Abstr.*, 1904, ii, 419.

Gismondite.—The formula of this mineral has been hitherto somewhat doubtful, but a specimen from the basalt of Nicolstadt, near Liegnitz, analysed by A. Sachs,[1] gives results which agree well with $(Ca,Na_2,K_2)Al_2Si_2O_8,4H_2O$, the formula proposed by Zambonini.

Glaserite.—The nature of this mineral has been the subject of a paper by B. Gossner.[2] He points out that conflicting views have been held by Retgers and van't Hoff, the former regarding glaserite as a double salt of the formula $K_3Na(SO_4)_2$, the latter considering it to be an isomorphous mixture of hexagonal modifications of the components. Gossner has studied the specific gravity, crystallography, and chemical composition of the products obtained under various conditions from solution of the sulphates and corresponding chromates respectively, and comes to the conclusion that Retger's view is the correct one.

Halloysite.—The pink clay from Pala, San Diego Co., California, has been shown by W. T. Schaller[3] to have the formula $H_4Al_2Si_2O_9,H_2O$.

Ilmenite.—A careful determination of the axial ratios, specific gravity, and chemical composition of specimens of this mineral from various localities has been made by G. Doby and G. Melczer.[4] The results are as follows:

Locality.	Axial ratio, $a : c$.	Sp. gr.	TiO_2.	FeO.	Fe_2O_3.	CaO.	MgO.	Total.
Snarum	1 : 1·368	5·041	5·66	0·11	93·50	—	1·10	100·37
Tvedestrand ...	1 : 1·3716	4·910	21·58	8·04	70·39	—	—	100·01
Ilmen Mts.....	1 : 1·3772	4·852	47·68	19·70	33·90	—	0·35	101·63
Kragero	1 : 1·379	4·614	49·68	15·72	34·51	0·07	—	99·98

It will be noticed that as the percentage of TiO_2 increases, the c axis becomes longer and the specific gravity diminishes.

Kunzite.—The composition of this variety of spodumene, remarkable for its power of responding readily to radium radiation, has been carefully investigated by R. O. E. Davies.[5] Analysis of very pure material gave:

SiO_2.	Al_2O_3.	NiO.	MnO.	ZnO.	CaO.	K_2O.	Na_2O.	Li_2O.	Loss on ignition.	Total.
64·05	27·30	0·06	0·11	0·44	0·80	0·06	0·30	6·88	0·15	100·15

These numbers agree with the formula $LiAl(SiO_3)_2$. The following elements were tested for with negative results: Mg, Cr, U, Ti, Fe, Sr, Ba, Th, Zr, Ce, Y, P. There appears to be nothing in the composition of the mineral to suggest an explanation of its unique properties.

Lawsonite, from Marin Co., California, has been the subject of a careful crystallographic and chemical study by T. Schaller and

[1] *Centr. Min.*, 1904, 215; *Abstr.*, 1904, ii, 420.
[2] *Zeit. Kryst. Min.*, 1904, **39**, 155.
[3] *Amer. J. Sci.*, 1904, **17**, 191; *Abstr.*, 1904, ii, 348.
[4] *Zeit. Kryst. Min.*, 1904, **39**, 526; *Abstr.*, 1904, ii, 666.
[5] *Amer. J. Sci.*, 1904, **18**, 29; *Abstr.*, 1904, ii, 621.

W. F. Hillebrand.[1] The mineral, which crystallises in the orthorhombic system, is essentially $H_4CaAl_2Si_2O_{10}$, some aluminium being replaced by ferric iron and some calcium by iron, magnesium, and potassium. A little titanium is also present.

Lorandite.—New analyses of this interesting thallium mineral have been made by P. Jannasch,[2] and by J. Loczka.[3] The results establish the formula $TlAsS_2$.

Mamanite.—This mineral, found at Maman, in Persia, was described by Goebel, who attributed to it the formula

$$3CaSO_4,K_2SO_4,2MgSO_4,3H_2O.$$

Van't Hoff having failed to obtain it synthetically in the course of his researches on oceanic salt deposits, has made, in conjunction with G. L. Voerman,[4] a new analysis of carefully selected material from the original locality. He concludes that mamanite is identical with polyhalite, $2CaSO_4,K_2SO_4,MgSO_4,2H_2O$.

Mispickel.—Crystals from Sulitjelma, in Arctic Norway, have been measured by M. Fletcher.[5] The axial ratios suggested glaucodote, but the analytical results obtained by J. A. Smythe indicate cobaltiferous mispickel:

	S.	As.	Fe.	CO.	Total.
I.	21·76	42·20	35·31	1·32	100·59
II.	21·96	42·15	36·17	0·98	101·26

Pyrochlore.—Analyses of a Scandinavian variety of this mineral, and also of the ilmenite and zircon which accompany it, have been published by G. P. Tschernik.[6]

Realgar.—Pure specimens from Allchar, in Macedonia, and from the Binnenthal, in Switzerland, have been analysed by P. Jannasch.[7] The numbers obtained agree very closely with those required by the formula AsS.

Rhodonite.—Dark red crystals, very rich in faces, have been described by L Colomba[8] from S. Marcel (Valle d'Aosta). The analytical results may be represented by the formula $7MnSiO_3,CaSiO_3$.

Sapphirine.—A rock composed of hypersthene, sapphirine, biotite, and hercynite is found in the Vizagapatam district of India. The sapphirine has been analysed by T. R. Blyth,[9] who deduces the

[1] *Amer. J. Sci.*, 1904, **17**, 195; *Abstr.*, 1904, ii, 350. See also F. Zambonini, *Atti R. Accad. Lincei*, 1904, **13**, ii, 466.

[2] *Zeit. Kryst. Min.*, 1904, **39**, 122; *Abstr.*, 1904, ii, 416.

[3] *Zeit. Kryst. Min.*, 1904, **39**, 520; *Abstr.*, 1904, ii, 666.

[4] *Sitzungsber. K. Akad. Wiss., Berlin*, 1904, 984; *Abstr.*, 1904, ii, 570.

[5] *Min. Mag.*, 1904, **14**, 54; *Abstr.*, 1904, ii, 743.

[6] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 712; *Abstr.*, 1904, ii, 620.

[7] *Zeit. Kryst. Min.*, 1904, **39**, 114; *Abstr.*, 1904, ii, 416.

[8] *Atti R. Accad. Sci. Torino*, 1904, **39**, 664; *Abstr.*, 1904, ii, 571.

[9] *Records Geol. Survey, India*, 1904, **31**, 38; *Abstr.*, 1904, ii, 668.

formula $MgO,2FeO,6Al_2O_3,2SiO_2$ from his results. Sapphirine having the composition $5MgO,6Al_2O_3,2SiO_2$ (a small part of the MgO being replaced by FeO) has been previously described from Greenland. It will be noticed that the relative amount of oxides of the type R″O is less in the Indian than in the Greenland specimen, while the proportion of FeO is much larger.

Schizolite.—A fresh examination of this mineral has been made by O. B. Böggild.[1] The rose-red to dark brown crystals belong to the anorthic system, and the formula $9SiO_2,6R''O,2(Na,H)_2O$ is deduced from the following analysis by C. Christensen:

SiO_2.	TiO_2.	Ce_2O_3.	Y_2O_3.	FeO.	MnO.	CaO.	Na_2O.	H_2O.
51·06	0·62	0·94	1·03	2·74	9·84	22·89	9·97	0·55

Böggild, however, after discussing two earlier analyses of the same mineral, suggests the simpler formula $3SiO_2,2RO(Na,H)_2O$, which has, moreover, the advantage of exhibiting the relation to pectolite.

Sodalite.—A remarkable occurrence of this mineral has been reported from Kishengarh, Rajputana, where it occurs in masses up to a foot across in veins of elæolite-pegmatite. The following analysis is by E. W. Vrendenburg:[2]

SiO_2.	Al_2O_3.	CaO.	Na_2O.	Cl.	Loss on ignition.
38·055	31·30	0·001	24·77	7·18	0·82

Traces of Fe_2O_3 and SO_3 were also found.

The mineral is either bright blue or colourless, its specific gravity is 2·27. The colourless variety, when kept in the dark for some time, turns pink, but loses the tint again when exposed to light.

Tetrahedrite.—An analysis of a specimen from Bocchegianno has been published by E. Tacconi.[3]

S.	Sb.	Cu.	Ag.	Fe.	Zn.	Total.
23·41	27·73	30·69	6·62	3·47	6·89	98·81.

Traces of As and Mn were also indicated.

As the analyst points out, the interest of the determination lies in the fact that the results can be easily interpreted by aid of the formula proposed for fahlerz (tetrahedrite) by Prior and Spencer in 1899, which in this case would be written as follows:

$$3(Cu,Ag)_2S,Sb_2S_3 + \tfrac{1}{4}[6(Zn,Fe)S,Sb_2S_3].$$

Another specimen from Palmavexi, Sardinia, analysed by C. Rimatori,[4] gave numbers agreeing with the simple formula $4Cu_2S,Sb_2S_3$.

[1] *Meddel. om Grönland*, 1904, **26**, 93; *Abstr.*, 1904, ii, 49.
[2] *Records Geol. Survey, India*, 1904, **31**, 43; *Abstr.*, 1904, ii, 667.
[3] *Atti R. Accad. Lincei*, 1904, **13**, i, 337.
[4] *Rivista Min.*, 1904, **31**, 46.

Thuringite and chamosite from the deposits of iron-ore in the Lower Silurian of Thuringia have been the object of an elaborate investigation by E. R. Zalinski.[1] The analytical results agree with the accepted formula of thuringite, $H_{18}(Fe,Mg)_8(Al,Fe)_8Si_6O_{41}$.

Titanium Olivine.—Specimens from Chiesa in Val Malenco have been described by L. Brugnatelli,[2] and analysed by Anelli. The numbers quoted below agree well with those given by material from Pfunders and Findelen, and lead to the orthosilicate formula $(H_2,Fe,Mg)_2(Si,Ti)O_4$.

Traces of fluorine and manganese are present, and the amount of water appears to be constant:

SiO_2.	TiO_2.	MgO.	FeO.	H_2O.	Total.
36·86	4·78	45·50	9·57	1·57	98·28

Topaz.—In a paper on the quantitative determination of fluorine, K. Daniel[3] gives reasons for assigning to topaz the following constitutional formula: $F_2{:}Si{<}^{O\cdot Al{:}O}_{O\cdot Al{:}O}$.

Vesuvianite.—Most of the crystals of this complex tetragonal silicate are optically negative. Those from Wilui, however, exhibit positive double refraction, while others are known with intermediate properties. Some years ago, Klein showed that similar phenomena observed in apophyllite appear to be connected with the amount of the volatile constituents, water and fluorine, present in the mineral. He has, therefore, examined the effect of heat on a large number of specimens of vesuvianite from different localities and finds that, with the exception of the positive crystals from Wilui, they all pass over into the normal negative type. Seeking for an explanation, Klein[4] has studied 83 analyses of vesuvianite, and concludes that the amount of water and fluorine are the determining factors, boron being of secondary importance.

Xenotime.—It has been suggested by Kraus and Reitinger that xenotime, YPO_4, is really a pseudomorph after hussakite, $3R_2O_3,3P_2O_5,SO_3$, sulphuric acid having been removed by the action of water. Brögger,[5] thinking this view improbable, caused some perfectly fresh xenotime from Arö to be tested for sulphuric acid. The result was negative, and Brögger therefore holds that xenotime is a definite mineral species, closely related morphologically to hussakite, to which he assigns the formula $5[YPO_4],[(SO_4,Y)PO_3]$.

[1] *Jahrb. Min.*, 1904, *Beil.-Bd.*, **19**, 40; *Abstr.*, 1904, ii, 571.
[2] *Zeit. Kryst. Min.*, 1904, **39**, 209. [3] *Zeit. anorg. Chem.*, 1904, **38**, 297.
[4] *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 653; *Abstr.*, 1904, ii, 668.
[5] *Nyt. Mag. Naturvidenskaberne*, 1904, **42** 1.

Artificial Formation of Minerals.

Phosphates, &c.—During the year, A. de Schulten[1] has continued his researches on the artificial production of phosphates, sulphates, and chromates, and has shown how hopeite, $Zn_3(PO_4)_2,4H_2O$, huréaulite, $H_2Mn_5(PO_4),4H_2O$, and crocosite, $PbCrO_4$, may be prepared in measurable crystals. To obtain hopeite, a solution of 45 grams of crystallised zinc sulphate in 500 c.c of water was mixed with 500 c.c. of a solution containing 37 grams of sodium phosphate, $Na_2HPO_4,12H_2O$. The precipitate which formed was dissolved in a slight excess of sulphuric acid, the solution kept warm on a water-bath, and very dilute ammonia (0·3 per cent.) allowed to drop slowly in (one or two drops per minute). At the end of eight days, a crop of good crystals up to 4 mm. long was obtained. A solution of manganese carbonate in phosphoric acid treated in a similar manner deposited huréaulite. Crocosite was formed when a dilute solution of potassium dichromate was dropped slowly into a warm solution of lead nitrate containing excess of nitric acid. A number of other phosphates, &c., not hitherto found as minerals, have also been prepared by similar methods.

Ruby.—An interesting account of the production of this crystalline form of corundum by fusion of alumina mixed with a little chromic oxide has been published by A. Verneuil.[2] The author employs a vertical blowpipe fed with coal gas and oxygen. The flame is directed downwards on to a support, the height of which can be slowly altered as the process proceeds. Alumina in a fine state of division is gradually introduced through the pipe which supplies the blast. By careful attention to a variety of details there may be obtained on the support a stick of alumina terminated by a spherical mass of crystalline transparent ruby.

Meteorites.

Catalogues of the important collections of the British Museum (by L. Fletcher), of the University of Berlin, and of the Ward-Coonley collection have recently appeared. Of these, the last is noteworthy as being now the most complete in existence, containing representatives of 603 different falls.

The following list contains the names of some interesting meteorites of which descriptions and analyses have been published during the year.

Cañon Diablo.—H. Moissan[3] has investigated the residue left

[1] *Bull. Soc. franç. Min.*, 1904, **27**, 97.
[2] *Ann. Chim. Phys.*, 1904, [viii], **3**, 20 ; *Nature*, 1904, **71**, 180.
[3] *Compt. rend.*, 1904, **139**, 773.

after dissolving 53 kilograms of this iron in hydrochloric acid. He finds that it contains amorphous carbon, graphite, and diamond, the latter both in rounded forms and in brilliant crystals.

Cañon City, Trinity Co., California.—An analysis of this iron is quoted by H. A. Ward.[1]

Casas Grandes, Mexico, is an octahedrite rich in taenite described by E. W. Cohen.[2]

Linum, Brandenburg, is a chondritic stone. An analysis by Lindner is given by Klein.[3]

Narraburra, New South Wales.—This iron has been analysed by A. Liversidge.[4]

Pavlovka, Russia, contains, according to Klein,[3] augite, bronzite, enstatite, olivine, anorthite, and perhaps leucite. It has been analysed by Lindner.

Peramiho, German East Africa.—This stone fell on October 24th, 1899. It consists of about 30 per cent. of anorthite and 70 per cent. of pyroxene, and is classified by F. Berwerth[5] as eukrite.

Persimmon Creek.—This is a meteoric iron of a somewhat unusual type. It has been examined by Wirt Tassin[6] and also by C. Klein. Tassin describes it as consisting of a more or less continuous metallic matrix in which are imbedded troilite, schreibersite, and carbon : small quantities of olivine are also found in the troilite areas. On treatment with dilute hydrochloric acid, sulphuretted hydrogen is evolved. Tassin has estimated the amount of this and has made analyses of the soluble portion as well as of the schreibersite, olivine, and insoluble taenite (Fe_6Ni). He classes the specimen as a granular octahedrite containing numerous areas of troilite and some of silicate. Klein[7] has identified rhombic and oblique pyroxenes in the dark silicate patches. He points out that this iron presents certain analogies to the irons from Kodaikanal and Netschaëvo, but thinks it is best placed in a class by itself.

Ranchito [*Bacubirito*], *Mexico.*—An iron consisting mainly of fine-grained plessite. It has been described by Cohen.[8]

Schafstädt, Merseburg.—This is a stone of considerable interest, as

[1] *Amer. J. Sci.*, 1904, **17**, 383.

[2] *Mitth. naturw. Ver. Neu-Vorpommern. v. Rügen*, 1904, **35**, (1903), 3 ; *Abstr.*, 1904, ii, 494.

[3] *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 114 ; *Abstr.*, 1904, ii, 352.

[4] *J. and Proc. Roy. Soc. New South Wales*, 1904, **37**, 234 ; *Abstr.*, 1904, ii, 671.

[5] *Tsch. Min. Mitth.*, 1904, **23**, 86.

[6] *Proc. U.S. National Museum*, 1904, **27**, 955 ; *Abstr.*, 1904, ii, 671.

[7] *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 572.

[8] *Mitth. naturw. Ver. Neu-Vorpommern. v. Rügen*, 1904, **35**, (1903), 3 ; *Abstr.*, 1904, ii, 494.

it has been shown by C. Klein[1] to contain leucite, a mineral not hitherto detected in meteorites. It fell in June, 1861, and its other constituents are anorthite, augite, glass, and ore.

Ternera, Chile.—An analysis of the iron is given by Klein.[1]

Toke-uchi-mura, Japan.—A meteoric stone. An analysis by Lindner is quoted by Klein.[1]

Toluca-Mani.—E. Sommerfeldt[2] has described a specimen from the Tübingen University Collection.

Uberaba, Minas Geraes.—E. Hussak[3] has given an account of this stone, which fell in 1903.

Weaver Mountain, Arizona.—A meteoric iron. An analysis by Lindner is quoted by Klein.[1]

Willamette, Oregon.—An octahedral iron, described by H. A. Ward.[4]

Rock Analyses.

Two valuable compilations have been issued by the United States Geological Survey. The first (Professional Paper No. 28) gives a series of "Superior analyses of igneous rocks," selected from Roth's Tabellen, 1869 to 1884, and arranged by H. S. Washington. The second, containing tables of 1672 analyses of rocks made in the laboratory of the United States geological survey between 1880 and 1903, has been compiled by F. W. Clarke[5] and issued as Bulletin No. 228. In an interesting introduction to this memoir, the mean composition of igneous rocks and the relative abundance of their constituent minerals is discussed, and the values deduced from the analyses tabulated. The general result arrived at is that the average igneous rock has very nearly metasilicate ratios and is quite close to an andesite in composition. The following figures give an approximate estimate of the relative abundance of the various minerals which enter into the composition of igneous rocks expressed in percentages: felspars, 59·5; hornblende and pyroxene, 16·8; quartz, 12; biotite, 3·8; titanium minerals, 1·5; apatite, 0·6. The less frequent minerals make up the residue, 5·8 per cent.

In this connection it is interesting to take note of the conclusion arrived at by Mennell[6] from a study of the distribution of igneous rocks in South Africa. He finds that granite so largely predominates that no appreciable error will be made if the average composition of

[1] *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 114, 978; *Abstr.*, 1904, ii, 352, 572.
[2] *Jahrb. Min.*, 1904, ii, 118.
[3] *Ann. naturhist. Hofmus. Wien.*, 1904, **19**, 85; *Abstr.*, 1904, ii, 746.
[4] *Proc. Rochester Acad. Sci.*, 1904, **4**, 137.
[5] *Abstr.*, 1904, ii, 669.
[6] *Geol. Mag.*, 1904, [v], **1**, 263.

the rocks of that region is taken to be the same as the mean composition of the granite. To take a mean of the values obtained on analysis of different rock types without regarding their relative abundance would in this case lead to quite erroneous results.

In conclusion, attention may be drawn to the "Manual of the Chemical Analysis of Rocks" (pp. ix. + 183. New York: Wiley and Sons; London: Chapman and Hall, Ltd., 1904) brought out by H. S. Washington. This work contains detailed instructions for carrying out the processes best suited to the analysis of complex silicates, and will be found invaluable by students of mineralogical chemistry.

A. Hutchinson.

RADIOACTIVITY.

THE rapid growth of the science of radioactivity and the comparative newness of the field of work which it covers make it desirable that the first annual report in this section should consist of a general *résumé* of the present position which has been attained. It is, however, impossible in the short space available to attempt to deal at all comprehensively with the many independent lines along which progress has been made. Since M. Henri Becquerel made the original discovery of radioactivity in the case of uranium in 1896, a mass of evidence has been accumulated rapidly by both physicists and chemists, and a volume could be filled by the mere enumeration of their results. Fortunately, this need not be here attempted, for during the past year several treatises have been issued which give connected accounts of the whole subject from the beginning. In recent discussions, the more purely physical aspects of radioactivity have received the greater attention, so that prominence will here be given mainly to the chemical evidence, and especially to the discovery of radioactive change and to the view that has been advanced that radioactivity is accompanied by the spontaneous transmutation of the radioactive matter.

It has been known from the first that radioactivity appeared to be a specific property of certain elements, and was independent of the physical or chemical condition of the substance. Becquerel showed that radioactivity, then defined as the power of giving out a peculiar radiation resembling the X-rays in its power of penetrating opaque matter and affecting the photographic plate, was a property common to all the compounds of uranium and to the element itself. Mme. Curie found that the activity of various uranium compounds was independent of their source or previous history and could not be increased or diminished by chemical treatment. She expressed the view that radioactivity was an atomic phenomenon, and later stated that this was the guiding principle underlying her researches. An examination of all the known elements showed that only one other, thorium, was radioactive, and this to about the same extent as uranium, when examined by the electrical method. To the photographic plate

thorium is much less active than uranium, and this is now explained by the fact that the intensity of the α-radiations, which cause the greater part of the electrical effect, is the same in the two cases, whilst the β-rays which cause the photographic effect are relatively feeble in the case of thorium. An examination of the naturally occurring minerals showed that many of the uranium ores possessed a higher activity than pure uranium or thorium compounds. On Mme. Curie's view of the atomic character of radioactivity, this could only be explained by the presence of unknown elements of great radioactivity, for it was not to be expected that any large proportion of new elements could be present in such well known ores. The successful search for these new elements in the pitchblende of Joachimsthal, Bohemia, is well known, and attention may be merely directed here to the striking confirmation it afforded of Mme. Curie's principle. Crookes later succeeded in profoundly modifying the activity of uranium by chemical treatment, thus showing that the principle had been originally based on erroneous evidence. But by that time the nature of the radioactive process was beginning to be elucidated, and the view that radioactivity is an atomic phenomenon in a modified and definite form still serves as the guiding principle of the investigator. It has served to explain and correlate the whole subject on a definite physical basis, and has directly suggested many fruitful researches.

In the early stages of the search for the unknown radio-elements causing the high activity of pitchblende, the mineral was separated into its constituents by the ordinary methods of chemical analysis, and the activity of each taken as the guide of the presence or absence of the active elements.[1] In this way, it was found that the active matter present, after the removal of the uranium, could be divided into three groups, the first separating with the bismuth (polonium), a second separating with the barium (radium), and a third discovered later by Debierne, separating with the rare earths (actinium). The justification for regarding the activity of pitchblende as being due to three distinct new elements rested at first entirely on the differences exhibited by the active matter in the analytical separation. Now, however, the claim is firmly based on the distinct specific character of the radioactivity in each case. It is difficult to give a concise answer to the question whether actinium and polonium are to be regarded as new elements. All the radioactive substances known exist in pitchblende. Of the eighteen given in a table later, sixteen are new. But in the case of one only, namely, radium, is there direct evidence of a material character of the specific elementary nature of the substance. In the other cases, such evidence is lacking, for all exist in such

[1] Mme. Curie, Thesis reprinted from *Chem. News*, 1903.

minute quantity that, apart from the radioactivity, there is no other evidence of their existence. The radioactive evidence is, however, of a very full and varied character, and the analogies existing between radium, the elementary character of which is beyond question, and the other radioactive substances, especially actinium and polonium, indicate that the sole reason why a specific material nature has not been shown to be possessed in the other cases is that the quantities dealt with are too small to come within the range of ordinary methods of examination.

Polonium.—Mme. Curie did not succeed in separating this substance from bismuth, although she effected a partial separation. Polonium is to be identified with the radio-tellurium of Marckwald, and to the latter we are indebted for the most definite chemical examination of the substance. In a series of remarkable investigations, Marckwald[1] effected the separation of polonium from bismuth, and attained to a degree of concentration of the radioactive matter far exceeding that necessary in the preparation of pure radium compounds. If a plate of bismuth is immersed in a solution containing polonium, the whole of the active matter is quickly deposited and the solution left inactive. The deposit is metallic in character and consists mainly of tellurium. A more advantageous separation may be effected by treating the solution with stannous chloride, when the whole of the active matter is obtained as a minute, intensely active precipitate. 1·5 grams of the latter were obtained by Marckwald from two tons of pitchblende. By the addition of hydrazine hydrochloride the whole of the tellurium was precipitated in the inactive state, the solution retaining the active matter. By the addition of stannous chloride, the latter was completely precipitated, the weight obtained being only four milligrams. This represents a proportion of one part to five hundred million parts of pitchblende. The quantity was too small to yield definite chemical reactions. The activity was, however, enormous. A hundredth of a milligram excites zinc sulphide to phosphorescence sufficiently intense to be visible to a large audience. Copper and bismuth plates coated with infinitesimal quantities of polonium, but extremely active, have been for some time on the market under the name of radio tellurium. Even the most powerful preparations of polonium are non-luminous. The radiation consists entirely of the α or non-penetrating type. No emanation is given off and polonium does not impart activity to surrounding objects.

Mme. Curie observed that the activity of polonium is not permanent, but decays steadily with the lapse of time.[2] The rate of decay has not yet been accurately determined, but the time taken for the activity to

[1] *Ber.*, 1902, **35**, 2285 and 4239; 1903, **36**, 2662.

[2] Thesis, p. 22 (translation).

fall to half the initial value is of the order of one year. The view now held is that it is probably a product of radium—the radium E of Rutherford.

Actinium.[1]—With this substance is to be identified the emanation substance or emanium described by Giesel.[2] Debierne, who discovered it in the rare earths separated from pitchblende, showed that the bulk of the matter consisted of thorium. Giesel succeeded in freeing his preparations from thorium and found the residue to consist mainly of lanthanum. Its radioactive properties have only recently been exactly studied. It gives both α- and β-rays, and Debierne showed that it gives a characteristic emanation, and imparts activity to neighbouring objects. These facts establish the claim of actinium to be considered as a specific type of radioactive matter. In all probability, actinium and polonium have each been obtained homogeneous in a radioactive sense, that is, they have been completely freed from other radioactive matter. But the proportion in which they exist in pitchblende is so minute that it is impossible to obtain a weighable quantity of either. It therefore follows that the activity must be exceedingly great, and in each case, comparing similar weights of matter, it is probably many hundred times the activity of pure radium. A practical difficulty in the way of their preparation is that they are undergoing change into inactive elements so rapidly that a limit is set on the amount that can be accumulated. The presence of inactive matter does not interfere with the investigation of their radioactivity, and in a radioactive sense actinium and polonium are now almost as well known as radium.[3]

Radium.—The barium obtained from pitchblende was converted into chloride and fractionally crystallised from water.[4] By arranging that only a small quantity of crystals separated from the solution, it was found that five times as much radium separated with the crystals as was left dissolved in the solution. By repeating this process a great number of times, Mme. Curie isolated from one ton of pitchblende residues (the residues left after the extraction of the uranium) a small fraction of a gram of pure radium chloride. When examined in the spectroscope, the brightest lines of barium were barely visible. The methods of fractionation have been improved by Giesel[5] by the substitution of the bromide for the chloride. Here also the radium tends to separate with the less soluble portion, but only about eight fractionations serve to remove the greater part of the barium. The

[1] Debierne, *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 906; 1903, **136**, 446 and 767.

[2] Giesel, *Ber.*, 1902, **35**, 3608; 1903, **36**, 342; 1904, **37**, 1696 and 3963.

[3] Compare Debierne, *Compt. rend.*, 1904, **138**, 411; Miss Brooks, *Phil. Mag.*, 1904, [vi], **8**, 382.

[4] Mme. Curie, Thesis, p. 24.

[5] *Ber.*, 1902, **35**, 3609.

yield stated by Giesel is about 0·2—0·3 gram of radium bromide from a ton of residues.

So obtained, the activity is about two million times as great as that of uranium, although a direct comparison of two activities so widely different is probably not very exact. The best preparations are but slightly luminous in the dark. The rays from a few milligrams, after penetrating an inch of steel, should produce an effect on an ordinary X-ray screen which should be immediately visible to a normally sensitive eye on completely darkening the room. This serves as a rough test of the genuineness of the product. The rays penetrating ordinary metal foil produce intense luminescence in barium platinocyanide crystals, willemite (zinc orthosilicate), and to a lesser degree in glass, paper, finger nails and many common materials. The radiations rapidly discolour glass and many salts in the same way as the cathode rays and X-rays. Quartz also undergoes slight darkening by prolonged action. Yellow phosphorus is converted into the red variety, and a solution of iodoform is turned purple by the action of the rays. Aqueous solutions of radium were found by Giesel to evolve hydrogen and oxygen continuously in considerable quantities. Radium produces physiological effects analogous to those produced by the X-rays. A few milligrams of radium bromide covered with thin mica and laid for a few minutes on the skin produce a painful burn which slowly develops and may take months to heal. The rays of radium have been used by medical men with marked success in the treatment of some forms of surface cancer, such as rodent ulcer, but they seem powerless to mitigate the ravages of deep-seated tumours.

The evidence for considering radium to be a new element is of the same character and at least as definite as in the case of any of the older known elements. In the first place, the methods of fractionation employed in its separation from barium show that it resembles the latter element almost completely, being distinguished only in its chemical reactions by the greater insolubility of its halide salts. The atomic weight of the element was obtained by Mme. Curie[1] from a determination of the percentage of chlorine in the anhydrous chloride, and found to be about 225. This agrees well with its chemical behaviour, for there is a vacant place in the periodic table corresponding with this value in the alkaline-earth family of elements. There is thus little doubt that radium is the missing heaviest representative of this family. Its whole behaviour conforms to this view. As in the case of the other members, it is most easily recognised by its flame and spark spectrum reactions, giving a fine carmine coloration to the Bunsen flame, and a most characteristic series of new lines in its spark spectrum. It was by the latter test that the first indication of its

[1] Thesis, p. 26.

presence, independently of the high radioactivity of preparations containing it, was obtained. The spectrum of radium has been studied exhaustively by Demarçay, Runge,[1] and Crookes,[2] the latter extending our knowledge into the ultra-violet region. The results of Runge and Precht[3] are highly interesting, for they examined the spectrum in a magnetic field in the same way as Runge had previously examined the spectra of the other alkaline-earth elements. Under these conditions, the spectrum may be analysed into several groups or "series," the members of the same series being resolved into components by the action of the magnetic field in a similar way. In this way, the lines of different series may be distinguished from one another. They separated the spectrum of radium into three separate series, which are exactly analogous in character to those previously distinguished in the case of calcium, barium, and strontium. By making use of an empirical relation, which has been found to hold for the other members of the family, connecting the constant difference in wave frequency between the individual lines of the same series and the atomic weight of the element, they deduced from the known values in the case of calcium, barium, and strontium the value 258 for the atomic weight of radium. This result is probably more reliable than that obtained, also from spectroscopic considerations, at about the same time by Marshall Watts.[4] The value obtained by this investigator agrees well with Mme. Curie's number, but according to Runge it was obtained by comparing together lines in different series. The discrepancy between the chemical and Runge's spectroscopic value for the atomic weight is of importance as it raises the question whether radium possesses a heavier or lighter atom than uranium. The higher number gives radium the heaviest atom known, whereas there are grounds for believing that radium is a product of uranium. The balance of all the evidence at the present time seems to be in favour of Mme. Curie's value. The well-defined material properties of radium, and especially the spectroscopic evidence, show that radium is as distinct and definite a type of elementary matter as any of the older known elements, and furnish a sufficient answer to the suggestion that radium is a compound, using that term in its ordinary chemical significance.

The property of radioactivity furnishes a new weapon for the detection of almost infinitesimal quantities of matter, and in this respect is almost incomparably more delicate than the spectroscope. Demarçay classed radium as an element giving an exceedingly delicate spectrum reaction, one part of radium being capable of detection by the spectroscope when mixed with 10,000 parts of barium. On the other hand,

[1] *Ann. Physik.*, 1903, [iv], **10**, 655, and **12**, 407.
[2] *Proc. Roy. Soc.*, 1903, **72**, 295.
[3] *Phil. Mag.*, 1903, [vi], **5**, 476. *Ibid.*, **6**, 64.

by the radioactive test, using the characteristic radium emanation, far smaller proportions can be measured. In recent experiments, the author has measured the amount of radium mixed with 10^{13} times the quantity of uranium, when the actual amount of radium was below 10^{-9} gram.

The present refined methods of investigation, introduced by Rutherford, have shown that no two of the known radio-elements exhibit the same kind of radioactivity, so that it is possible to distinguish uranium, thorium, radium, polonium, or actinium from one another by their radioactivity, even when they are only present in excessively minute quantity. Hence the activity of any two or more of these elements cannot be due to the presence of a common constituent. The electrical methods of measurement are capable of great range, accuracy, and rapidity, and have, except in special cases, almost entirely replaced the older photographic method by which Becquerel originally discovered the uranium radiation. They depend on the fact that the newly-discovered types of radiation, the X-rays, cathode rays, and the α-, β-, and γ-rays of the radio-elements possess in common the power of converting, for the time being, the gases through which they pass into partial conductors of electricity. The conduction of electricity through gases exposed to the X-rays was shown by J. J. Thomson[1] to be effected by a similar mechanism to that obtaining in liquid electrolysis. The current is conveyed by the convection of oppositely charged molecules or ions to the respective electrodes. But there is a well-marked distinction. Electrolytes are now regarded as existing in a permanently ionised condition, and even in the case of very non-conducting liquids the number of ions present, whether the current is acting or not, is always very great compared to the number discharged in unit time at the electrode. Hence electrolytes obey Ohm's law. In the case of gases screened from the action of ionising radiations it is probable that no ions exist. The ionising rays produce the ions throughout the volume of the gas in very limited numbers, the number produced in unit time being a measure of the intensity of the radiation absorbed by the gas. Hence conducting gases do not obey Ohm's law, but above a certain critical difference of potential between the two electrodes, known as the "saturating voltage," the current flowing is independent of the voltage. Owing to the small viscosity of the gas compared with that of a liquid, the movement of the ions is much more rapid in gases, and is of the order of 1 cm. per second for unit potential gradient in air. When the ionising agency is withdrawn, the oppositely charged gaseous ions rapidly recombine, and the gas again assumes the non-conducting state. The tendency towards recombination always exists. The

[1] Conduction of Electricity through Gases, 1903.

maximum current capable of flowing through a gas, known as the "saturation current," serves as an accurate measure of the number of ions produced in unit time, and is proportional to the amount of radiation absorbed by the gas. It may be defined as the current flowing when all the ions present give up their charges to the electrodes, the proportion recombining in the volume of the gas before reaching the electrodes being inappreciable. In practice, for weak radioactive preparations, under the conditions ordinarily employed, 300 volts serves to produce the saturation current.

The current is usually measured by means of a quadrant electrometer. Very feeble currents are measured by the rate of discharge of a gold-leaf electroscope. The currents produced by active radium preparations may be measured by means of a sensitive galvanometer. M. Curie uses a special method of measurement, in which the electrometer is used as an indicator, the current flowing through the gas being balanced by an exactly equal and opposite current produced by tension of a lamina cut from a quartz crystal. This has all the advantages of a null method, and is independent of the sensitiveness of the electrometer.

Professor J. J. Thomson's theory of gaseous conduction was shown to apply without modification to the ionisation effected by the rays of uranium and the other radio-elements.[1] In this research, Rutherford analysed the radiation of uranium into two types, the α-radiation, which produces by far the greater part of the ionisation, and is absorbed by a single sheet of ordinary paper, and a β-radiation producing relatively feeble ionisation, but capable of traversing a thickness of several millimetres of aluminium, copper, glass, &c., before being completely absorbed. This method of analysing the complex radiations given out by the radio-elements, by the successive absorption of the less penetrating types, has been widely used in the case of the other radio-elements, and forms one of the two main methods used for this purpose. The other depends on the effect of an electric and of a magnetic field on the path of the ray. Both methods agree in distinguishing three distinct classes of rays, the α- and β-rays already mentioned and a third relatively unimportant type called the γ-rays.

γ-Rays.—These are characterised by their extraordinary power of penetration. According to the measurements of Rutherford,[2] 1 per cent. of the γ-rays survive absorption after penetrating 7 cm. of lead, 19 cm. of iron, or 150 cm. of water. The γ-rays from uranium and thorium are hardly detectable unless large quantities of these substances are examined. Those from radium are fairly prominent, both

[1] Rutherford, *Phil. Mag.* 1899, [v], **47**, 109.
[2] *Nature*, 1902, **66**, 318.

by their photographic and fluorescence effects. Their ionising power is relatively feeble, owing to the slight extent to which they are absorbed by gases. They are not deviated by the most powerful electric or magnetic fields, and in this they resemble the X-rays. Although considerable differences exist between ordinary X-rays and the γ-rays in their relative powers of ionising different gases, A. S. Eve [1] has shown that the latter are similar in these respects to the most penetrating X-rays that can be produced. Rutherford has shown that the production of the γ-ray is causally connected with the expulsion of the β-particle, the two types of radiation always being proportional to one another. The view [2] is now generally held that the γ-ray stands in the same or a similar relation to the β-ray as the X-ray stands to the cathode ray. The main difference is that the γ-rays are produced by the sudden positive acceleration of the electron which constitutes the β-radiant particle, whereas the X-rays are produced by the far less sudden negative acceleration undergone by the cathode radiant particle on collision with the anticathode of the X-ray bulb. The much greater penetrative power of the γ-ray is simply explained by the far greater acceleration experienced by the electron in the disintegration of the atom than can be effected by any artificial process.

β-Rays.—This type was at first the most studied. It produces relatively small ionisation, but powerful fluorescence and photographic action. The author has shown [3] that the whole of the photographic effect of uranium is due to the β-rays alone. The phosphorescence of the platinocyanides, willemite, and kunzite in ordinary circumstances is mainly due to the β-rays. On the other hand, zinc sulphide is but little affected by this type.

The β-rays were identified early with the cathode rays, or radiant matter of Sir William Crookes, for they readily suffer deviation by electrostatic and magnetic fields in the same sense as the cathode ray, although not nearly so readily as the latter. The views held originally by Crookes of the corpuscular nature of the cathode radiation have been proved and extended by J. J. Thomson, and the latter's well-known theory [4] with regard to their nature is now universally accepted by physicists. By simultaneous measurements of the electrostatic and magnetic deviation suffered by the cathode radiant particle, Thomson deduced their velocity and ratio e/m, of the charge e to the mass m. The velocity increases with the degree of exhaustion of the Crookes tube, and for high exhaustion averages one-tenth, and may attain one-third of the speed of light. The ratio

[1] *Phil. Mag.*, 1904, [vi], **8**, 610.
[2] Rutherford, *Nature*, 1904, **69**, 436.
[3] *Trans*, 1902, **81**, 1860.
[4] Conduction of Electricity through Gases, 1903.

e/m, on the other hand, is invariable, being independent of the velocity, the nature of the material of which the cathode is made, the nature of the gas present in the tube, and the manner in which the cathode rays are produced. Thus the same value was obtained for the cathode rays expelled from a negatively-charged polished zinc surface *in vacuo* under the influence of ultra-violet light. This ratio was found to be one thousand times greater than in the case of the hydrogen ion of electrolysis, and therefore a thousand times greater than in any case previously observed. If ultra-violet light falls on zinc in a gas under atmospheric pressure, the ordinary negative ions of gaseous conduction are expelled. The charge carried by the individual ion has been directly determined and shown to be the invariable "atomic charge" carried in every case by the gaseous ion, and equal to that carried by the univalent ion in electrolysis. By diminution of the pressure of the gas, the free path of the expelled negative ion is increased, until at high exhaustions it is free to move under the action of the electric field, and then becomes a cathode ray particle. Hence, unless the charge suffers subdivision in this process to one-thousandth of its initial value, which on the atomic view of electricity now prevalent is hardly conceivable, it follows that the mass of the cathode radiant particle must be only one-thousandth of the mass of the hydrogen ion. The view now held is that the cathode radiant particle constitutes a single electron or atomic charge travelling free and unassociated with matter. This view will be alluded to later.

Becquerel[1] found that the ratio e/m of the β-radiant particle from radium and uranium is the same as in the other cases referred to. The velocity is in general far higher. The β-rays of uranium travel at about two-thirds the velocity of light, whilst in radium the velocity varies over a considerable range, but Kaufmann[2] has shown that the most penetrating β-rays of radium possess a velocity of 95 per cent. of that of light. Becquerel had shown previously that the least penetrating rays are the easiest to deflect and possess the lowest velocity. The direct proof that the β-rays transport negative electricity was obtained by M. and Mme. Curie, who showed that an insulated metal plate in the path of the β-rays of radium acquires a negative charge, although the rays were first made to traverse a sheet of thin metal connected to earth. The same effect has been shown in the simplest manner by Strutt,[3] whose apparatus is well known.

α-Rays.—These are distinguished by feeble penetrative power, feeble photographic effect, but very great ionising power. The latter is connected with their almost complete absorption by a few centimetres of air. Their phosphorescent effects are small in the case of those substances

[1] *Compt. rend.*, 1900, **130**, 809.
[2] *Ibid.*, 1902, **135**, 577.
[3] *Phil. Mag.*, 1903, [vi], **6**, 588.

which show the β-radiation well, but very great in the case of Sidot's hexagonal blende (phosphorescent zinc sulphide). It was discovered simultaneously by Sir William Crookes and by Elster and Geitel that the phosphorescence of zinc sulphide under the α-radiations, when resolved by a lens, consists of momentary flashes or scintillations. It is of interest to record that Elster and Geitel discovered this property for the radioactive matter separated from the atmosphere.[1] The well-known instrument designed by Crookes and known as the spinthariscope illustrates this effect in a simple manner. It is probable that each flash of light corresponds to an impact of the individual α-particle, so that the instrument may be said to render visible to the eye the effect of a single atom of matter. This thought brings out vividly the new relations between energy and matter which radioactivity has revealed. When it is considered that the quantity of radium used in the construction of the spinthariscope is probably quite unweighable, and that the effect persists over years without diminution (although the phosphorescent screen may need renewal), some idea may be obtained of the delicacy of the radioactive methods of investigation.

Rutherford recognised at a very early stage the preponderating importance of the α-rays, and showed that in all cases they represented by far the greater part of the total energy radiated. This view has received repeated confirmation. The nature of the α-rays for a long time remained unsettled, and they were at first thought to be the X-rays resulting from the expulsion of the β-rays. This view was advocated by Becquerel, but it is now known that the α- and β-radiations are quite unconnected.[2]

It has been shown that the two rays occur at quite different stages of the radioactive process, so that in the case of uranium it is possible to separate all the β-radiating matter from that giving the α-radiations. The nature of the α-rays was elucidated by Rutherford,[3] who succeeded after many failures in establishing that they undergo a slight but perceptible deviation by very intense electrostatic and magnetic fields. The deviation is in the opposite sense to the cathode-ray, and Rutherford concluded that the α-radiation, like the β-radiation, consists in the flight of discrete charged particles, which carry a positive instead of a negative charge. The idea, however, that the two processes are in any way complementary to one another does not bear criticism, for it is known that in most cases several α-particles are expelled from the atom before the β-particle is expelled.

Using reasoning similar to that originated by Thomson, Rutherford

[1] The radioactivity of the atmosphere seems to be derived from a minute amount of radium emanation diffusing from the soil. The latter appears frequently to contain infinitesimal quantities of radium.

[2] Soddy, *Trans.*, 1902, **81**, 1860.

[3] *Phil. Mag.*, 1903, [vi], **5**, 177.

deduced the value of the velocity of the α-particle to be about one-tenth of the speed of light, and the ratio e/m to be over one thousand times smaller than in the case of the β-particle. Making the assumption that the charge carried by the α-particle is the same as that carried by the univalent ion, Rutherford deduced the mass of the particle to be 1·6 times the mass of the hydrogen atom. The deviation has been confirmed by Becquerel,[1] who showed also that the α-ray of polonium is similarly deviated. Recent developments have caused Rutherford to consider it probable that the α-particle is or becomes an atom of helium.

New results have gone to show that there is still much to be explained with regard to the nature of the α-ray, for it seems proved that the α-particle at the moment of its expulsion is uncharged, but gains a positive charge by passage through the gas. This result transpired in consequence of the failure of all attempts to detect the positive charge carried by the α-rays by direct methods similar to those described for the case of the β-rays. On account of the easy absorption of the rays, and the need to avoid ionisation, it was necessary to perform the experiments in a very high vacuum. Wien,[2] working in this manner, showed that a plate exposed to the α-rays did not gain a positive charge, and Rutherford[3] has recently obtained the same result. On the other hand, it has been deduced from theoretical considerations by Bragg,[4] that even if the α-particle started on its course through a gaseous atmosphere uncharged it must immediately lose an electron by passage through the atom of the gas molecule, and so gain a positive charge. Ionisation is usually regarded as being due to the detachment of an electron from the atom of the gas molecule struck by the radiant particle. There is a fundamental difference, however, between the ionisation produced by a radiant electron or β-ray, and by a radiant atom or α-ray. In the latter case there is just as much reason for an electrically neutral α-radiant particle to suffer the loss of an electron and become positively charged as there is for the electrically neutral atom of the gas molecule struck by the α-particle. In other words, in the case of two colliding atoms, the ionisation must be mutual, for, so far as their relative motion is considered, either might be regarded as the radiant particle. This view, although only barely referred to in the paper quoted, is of considerable importance. The author[5] has drawn attention to the difficulty of explaining, on the current ideas with regard to the con-

[1] *Compt. rend.*, 1903, **136**, 199, 431, 1517.
[2] *Physikalische Zeitschrift*, 1903, **4**, 624.
[3] Bakerian Lecture, *Phil. Trans.*, 1904, **A204**, 213.
[4] *Phil. Mag.*, 1904, [vi], **8**, 721.
[5] Radioactivity, 1904, p. 180.

servation of opposite electric charges, the fact that the residue left from the electrically neutral atom on the expulsion of the positively charged α-particle is left positively charged (compare p. 258). On Professor Bragg's view, the positive charge in *both* cases is acquired after the disintegration, the recoil of the residue being considered to have the same effect as expulsion in the case of the radiant particle. Two consequences immediately follow: (1) in a perfect vacuum, the excited activity should not be concentrated on the negative electrode in an electric field. This fact has been observed by Rutherford [1] experimentally, but no explanation has before been given; (2) the α-particle in a vacuum should undergo neither electrostatic nor magnetic deviation. Des Coudres [2] has measured the electrostatic and magnetic deviation of the α-particle by Becquerel's photographic method in very high vacua, and has obtained identical results with those obtained by Rutherford, who worked in hydrogen under atmospheric pressure, by the electrical method. There is thus need for a careful re-examination of this question, for there is strong probability in favour of the view that the α-particle is initially uncharged, but gains its charge by the ordinary mechanism of ionisation. A further important advance in our knowledge of the α-rays of radium has been made by Bragg, and will be referred to after the subject of radioactive change has been considered.

Types of Temporarily Radioactive Matter.—The view that radioactivity is an atomic property necessitates, on the older view of the unchangeability of the atom, that the activity should be in all cases a permanent property of the matter exhibiting it. This is, however, far from being the case, for it is now known that in many of the cases of radioactivity, in addition to the expulsion of α- and β-particles, there is a simultaneous production of new types of matter possessing temporary radioactivity. The first of these to be discovered was the thorium emanation. Rutherford,[3] by the aid of the electrical method of investigation, found that the compounds of thorium differ from those of uranium in that they not only emit α- and β-rays, but also that they communicate to the surrounding atmosphere the property of temporary radioactivity. The air in the immediate neighbourhood of a thorium compound itself emits α-rays of a kind similar to those emitted by the thorium compound directly. For some minutes after removal, the air retains its radioactivity, but the latter continuously diminishes in a geometrical progression with the time. At the end of each minute interval, the activity is only one-half as great as at the beginning of the interval, so that in ten minutes the activity of the air is only one-thousandth of

[1] Radioactivity, 1904, p. 282.
[2] *Physikalische Zeitschrift*, 1903, **4**, 483.
[3] *Phil. Mag.*, 1900, [v], **49**, 1.

the initial, and may be neglected for practical purposes. If the thorium compound is wrapped in porous materials such as paper or thin metal leaf, the same effect is observed, but the thinnest sheet of mica, or other substance completely impervious to the passage of a gas, entirely prevents it, and the outside air shows no trace of self-radioactivity. Rutherford concluded that an actual material substance or "emanation" was given off by thorium compounds, and this emanation possessed the power of diffusing like a gas. Later work has established the view, and shown that the radioactive emanations given off by thorium, radium, and actinium are radioactive gases of high molecular weight, present in such minute amount that the radioactivity is usually the only indication of their existence. All thorium compounds show this property, but in widely varying degrees, the emanating power of thorium oxide being much diminished by strong ignition. But the emanation always presents the same characteristics, and its radio activity decays at the same rate under all conditions so far investigated. If the course of decay is represented by the equation

$$\frac{I_t}{I_o} = \epsilon^{-\lambda t},$$

where I_t is the activity after time t in seconds and I_o the initial activity, e being the base of natural logarithms, and λ a constant, it becomes general for all types of temporarily radioactive matter known. But the constant λ varies widely in the different cases and has received the special name of the *radioactive constant*. Thus for the thorium emanation it has a value of 1/87, when t is expressed in seconds. The radioactive constant is the most characteristic feature of a temporarily active type of matter, and serves well for its differentiation. According to the disintegration theory, it represents the fraction of the whole undergoing change per second, and the reciprocal $1/\lambda$ represents the average life of the changing atom in seconds.

Radium and actinium both give radioactive emanations, but uranium and polonium do not. The radium emanation loses its activity much less rapidly than that from thorium, but the course of decay follows the geometrical law given. The value of λ is here about 0·000002,[1] the activity falling to half the initial value every four days. The value of $1/\lambda$ is 5·3 days. The actinium emanation, on the other hand, is even shorter lived than that from thorium, the value of λ being 0·17, according to Debierne.

The three elements giving radioactive emanations are the only ones possessing the much-discussed property of inducing or exciting radioactivity in surrounding objects, or, to speak more accurately, of

[1] Curie, *Compt. rend.*, **1902**, **135**, 857 ; Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], **5**, 455.

imparting radioactivity to surrounding objects. This property was discovered in the case of thorium by Rutherford,[1] and at once correctly ascribed by him to the action of the emanation, and by M. and Mme. Curie[2] in the case of radium, and ascribed by Becquerel to a phenomenon analogous in nature to phosphorescence. Rutherford submitted the thorium-excited activity to a careful investigation. He showed that only those substances were rendered active by thorium which had come into immediate contact with the thorium emanation, and that the intensity of the radioactivity of the substance rendered active was proportional to the intensity of the radioactivity of the emanation in which it had been immersed. He showed that on removing the substance rendered active from the action of the emanation, the activity decayed in a geometrical progression with the time, falling to half the initial value in about 11 hours, and finally completely disappearing. The radiation from the substance rendered active consisted of both α- and β-rays of a similar kind to those given by the thorium directly, and was completely independent of the nature of the matter of which the object rendered active was composed. Moreover, it could be removed from the latter by scrubbing the surface with sand-paper and by the action of some acids. In neither case was the activity at all destroyed, but merely transferred to the sand-paper or acid. In the latter case, if the acid were evaporated, the activity remained on the dish used. The activity decayed at the same rate in the acid as on the substance originally rendered active. Rutherford concluded that, as in the case of the emanation, the radioactivity was caused by minute amounts of matter, which in this case were deposited from the emanation as a thin and invisible film over the surface of the substance rendered active.

He made the further important observation that in an electric field the excited activity produced by both the thorium and the radium emanation was entirely concentrated on the negative electrode and therefore was positively charged. By using a thin platinum wire for the negative electrode and making the rest of the containing vessel the positive electrode, he succeeded in making the wire intensely active. But no visible deposit was observed on the wire when examined under a high power microscope, and no gain of weight could be detected by a sensitive balance. He found that when the pressure of the atmosphere was diminished below 10 mm. the whole of the excited activity was not deposited on the electrode, while under 0·1 mm. pressure the amount deposited on the negative electrode was small. An explanation of this result has already been suggested (p. 256).

Becquerel,[3] to explain the excited or induced activity produced by radium, proposed the hypothesis of radioactive induction, which he

[1] *Phil. Mag.*, 1900, [v], **49**, 161. [2] *Compt. rend.*, 1899, **129**, 823.
[3] *Ibid.*, 1901, **133**, 977.

also employed to explain other cases of temporary radioactivity. According to this view, the radioactivity is induced in the originally inactive matter—the gas in the case of the emanation, the solid matter in the neighbourhood in the case of the excited or induced activity—by the *radiations* of the original radio-element, much in the same manner as phosphorescence is induced by exposure to light radiations. This view has been disproved by direct experiment. The radiations of the original radio-element do not cause any kind of matter to become radioactive. Exception must be made here in the case of an observation recorded by Sir William Ramsay and Cooke,[1] who found that the inside of a glass surface was rendered feebly active by exposure to the β-rays of radium. But the effect was very feeble, and of an entirely different order of magnitude to those dealt with in the case now considered. It has been established that the ordinary induced or excited activity of the three elements is only produced under conditions which allow of the direct transference of the radioactive emanation from the element to the substance rendered active. From the point of view of chemistry, the recognition of the material nature of the emanations and the other examples of temporary radioactivity possesses an importance that can hardly be over-estimated.

A closer investigation of the chemical and physical nature of the emanations was carried out by Rutherford and Soddy.[2] The emanations from radium and thorium may be led in tubes containing the most powerful reagents at high temperature, such as platinum black, copper oxide, zinc dust, without being absorbed or their activity sensibly affected by the process. The conclusion was drawn that the emanations were gases allied in nature to the members of the argon family and possessing the same power of resisting chemical combination as the latter. This conclusion was endorsed by Sir William Ramsay after some experiments conducted in conjunction with the author,[3] in which the radium emanation mixed with oxygen was subjected to prolonged sparking over caustic potash and mixed with air to prolonged contact with a heated mixture of magnesium and lime. In neither case was the emanation appreciably absorbed or the activity altered.

The discovery by Rutherford and Soddy that at low temperature both emanations are condensed,[4] and again assume the volatile form when the temperature is allowed to rise, finally established the material nature of the emanations beyond question. At $-154°$, the radium emanation condenses very sharply and completely, and is again volatilised completely if the temperature is allowed to rise only one or two degrees.

[1] *Nature*, 1904, **70**, 341.
[2] *Trans.*, 1902, **81**, 342.
[3] *Proc. Roy. Soc.*, 1903, **72**, 204.
[4] *Proc.*, 1902, **18**, 219; *Phil. Mag.*, 1903, [vi], **5**, 561.

Since pure radium compounds have become available, it is possible to obtain fluorescence effects with the emanation of sufficient magnitude to be plainly visible to large audiences, and the gaseous nature of the radium emanation, its passage through tubes, and condensation at the temperature of liquid air may be made the subject of many simple and striking lecture experiments. The condensation on fragments of willemite contained in a U-tube immersed in liquid air, according to the method originally employed by Rutherford, is an especially beautiful experiment. This property has also been of the greatest service in the isolation of the radium emanation in a pure state, with very fruitful results.

Although uranium does not give an emanation, it gives a temporarily radioactive type of matter which, except that it is not volatile at the ordinary temperature, and therefore must be separated by chemical methods, is very similar to the emanations from a radioactive point of view. Sir William Crookes found [1] that if crystallised uranium nitrate were dissolved in ether and the aqueous layer separated from the ethereal layer, the uranium oxide obtained from the latter was almost completely inactive to the photographic plate, whereas the relatively small quantity of uranium oxide obtained from the aqueous solution was intensely active to the photographic plate. Or, if ammonium carbonate is added to an aqueous solution of a uranium compound in excess so that the uranium carbonate is redissolved, the very small precipitate that is obtained on filtration possesses all the photographic activity of the original uranium, and, weight for weight, may be many thousand times as active as the latter. The uranium obtained from the solution is again completely inactive to the photographic plate. Crookes concluded that he had separated an active constituent responsible for the whole of the radioactivity of the uranium, and named it Uranium X.

Becquerel [2] independently obtained similar results, but made in addition the important observation that if the preparations were kept for a year the uranium completely regained its lost activity, while the uranium X completely lost its activity. These results he sought to explain by the hypothesis of radioactive induction already mentioned.

The author in a re-examination of these facts [3] found that by the methods of Crookes and Becquerel only the β-radioactivity of uranium had been separated. The preparations which Crookes, using only the photographic method, described as inactive were found to possess a nearly normal activity when tested by the electrical method, whereas the preparations of uranium X which were intensely active to the

[1] *Proc. Roy. Soc.*, 1900, **66**, 409.
[2] *Compt. rend.*, 1900, **131**, 137; 1901, **133**, 977.
[3] *Trans.*, 1902, **81**, 860.

photographic plate are only feebly active when examined by the electrical method. The processes of decay and recovery described by Becquerel refer only to the β-radioactivity. So far as is at present known the whole of the α-radioactivity is a specific or atomic property of the uranium.

Simultaneously with the work on uranium, Rutherford and Soddy[1] submitted the radioactivity of thorium to a careful chemical investigation. It was found that if a solution of thorium was precipitated by ammonium hydroxide, the thorium hydroxide was obtained very much less radioactive than before. By this method, the whole of the β-radioactivity may be removed and the α-radioactivity reduced to 25 per cent. of the normal. Moreover, the thorium hydroxide so obtained, whether examined in the solid state or in solution, possesses no emanating power at all. If the solution from which the thorium had been precipitated was examined, it was found to possess the whole of the emanating power possessed originally by the thorium. When evaporated to dryness, and the ammonium salts expelled by ignition, a minute residue only was left, but this possessed in concentrated form all the radioactivity which the thorium had lost in the process. Thus it gave β-radiation equal in amount and α-radiation to the extent of 75 per cent. of that given originally by the thorium preparation. The active constituent thus separated was named thorium X. Then it was found that the radioactivity of thorium X after separation rapidly decayed with time, and with the radioactivity the emanating power dimished correspondingly. Both processes followed the geometrical law of decay and proceeded at the same rate, both the emanating power and the radioactivity decaying to half the initial value after the lapse of 4 days. Concomitantly the thorium hydroxide, which when first precipitated possesses no emanating power, no β-activity, and 25 per cent. of its normal α-activity, gradually recovered both its radioactivity and emanating power, and after the lapse of three weeks was normal in every respect. The simple law was followed that the sum of the various activities of the two preparations was at all times equal to the activity of the thorium salt initially. Rutherford and Soddy obtained similar results in the case of uranium.[2] During the course of the decay of the β-activity of uranium X and the recovery of the β-activity by the uranium, the sum of the two activities is a constant. But here the rate of change is much slower than in the case of thorium. The activity of uranium X decays to half its initial value in about 22 days.

It was found that if the uranium and thorium preparations which had recovered their lost activity were again subjected to the same

[1] *Trans.*, 1902, **81**, 321, 837; *Phil. Mag.*, 1902, [vi], **4**, 378, 569.
[2] *Phil. Mag.*, 1903, [vi], **5**, 441.

process as at first, new amounts of thorium X and uranium X were obtained, and this process can be repeated an indefinite number of times with the same preparation. On the other hand, if the processes of separation follow one another without pause, no further amount of the active products can be separated after the first amount.

The evidence in favour of regarding thorium X and uranium X as new specific types of matter in too small quantity to be detected except by their activity is as strong as in the case of the radioactive emanations, or in the case of polonium or actinium. Each possesses a well-defined behaviour. Thus the separation of thorium X from thorium can only be effected if ammonium hydroxide is used as the precipitant. If sodium hydroxide or ammonium carbonate or oxalate is employed to precipitate the thorium, no separation is effected, the precipitated thorium is in its normally active state, and the filtrate contains no radioactive matter. The behaviour is not therefore to be ascribed to the mere process of precipitation, but can only have a chemical explanation, namely, that part of the activity of thorium is due to the presence of a non-thorium type of matter, differing from thorium in chemical nature and so capable of separation. The actual amount is, as in the case of the emanations, so minute that it can only be detected by means of its radioactivity. From these results, Rutherford and Soddy advanced the view that there is a continuous production of uranium X and thorium X from uranium and thorium. It was found that the rate of decay of the activity of uranium X and thorium X was completely independent of temperature and of chemical treatment. The activity of these substances must be regarded as always decaying at the same rate whether they are separated from the element producing them or not. The constancy of the radioactivity of uranium and thorium is thus only apparent and is due to the equilibrium between two opposed processes. After separation, the activity of the thorium increases until the increase of activity due to the steady production of fresh thorium X is balanced by the decay of the activity of that already formed. This state has been termed *radioactive equilibrium*. When attained, the activity appears to be constant and permanent. The chemical separation thus only reveals the dual character of the radioactive process without in any way interfering with its course.

The effect of various conditions on the radioactive process has been studied in many cases, but most completely for the radioactive emanations of radium and thorium.[1] These lose their activity at the same rate at a red heat as at the temperature of liquid air, and are unaffected by chemical treatment. Rutherford and Soddy con-

[1] Curie, *Compt. rend.*, 1902, **135**, 857; Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], **5**, 561.

cluded[1] that the continuous production of thorium X from thorium and of uranium X from uranium is due to the change of the uranium or thorium atom, for the rate of production depends only on the quantity of element, and if it were merely a molecular change it should be dependent on molecular conditions

It is impossible by chemical processes to remove entirely the activity from either thorium, uranium, or radium. A *non-separable activity* always remains, and in each case consists only of α-rays. The whole of the α-radiation of uranium, and 25 per cent. in the other two cases, constitutes the non-separable activity. The radioactivity of these elements therefore consists of two atomic phenomena simultaneously occurring. It is now known that this holds true in all cases. For just as the non-separable activity of thorium occurs with the production of thorium X, the activity of the latter and the production of the emanation are connected, the power of producing an emanation not being possessed by thorium, but only by thorium X. In the next stage, the activity of the emanation is associated with the production of the matter, often referred to as the "active deposit," which is the cause of the excited activity. From the fact that the two processes are always proportional, it was deduced that the change of the atom into the new atom was accompanied by the expulsion of the radiant particle. It is, in addition, a sufficient explanation of the cause of the change, for on generally accepted chemical ideas the expulsion of a mass of the size of the α-particle from an atom would have the effect of completely altering its chemical nature, and would be of a sufficiently fundamental character to account for the complete transformation which the matter undergoes in its passage from thorium into thorium X, from the latter into the inert gaseous emanation, and then back again into a non-volatile form. This view derives great support from a consideration of the physical interpretation to be put on the geometrical decrease of the activity in the case of the intermediate or transition forms produced in the series of changes. In the original change, so small a fraction of the thorium changes in unit time that the quantity is not appreciably diminished. Hence the changing fraction remains a constant definite quantity, and the number of radiant particles expelled in unit time, or the non-separable activity, and also the number of new thorium X atoms produced remains constant. This, however, carries with it the necessary consequence that the actual number of thorium X atoms formed in any period of observation must be practically infinitesimal, and far below direct methods of investigation. But the only condition for its detection by radioactive methods is that a sufficient number of α-particles must be expelled in unit time. It is probable from considerations mentioned in connection with

[1] Radioactive Change, *Phil. Mag.*, 1903, [vi], 5, 576.

the spinthariscope that a very small number can be detected, but since the total quantity is practically infinitesimal, even a small number must represent a finite fraction of the total. Hence the amount present must appreciably diminish, and the activity of thorium X will decay with the time, and, proportionately, the production of emanation will diminish.

It is well known that the character of a chemical change can be deduced from a study of the rate of change. Thus Wilhelmy showed that in the case of a unimolecular reaction the amount of changing substance present diminishes in a geometrical progression with the time. This is also the law of radioactive change, for the radioactivity is a direct measure of the number of atoms changing, and of the proportion remaining unchanged. For the so-called permanently radioactive elements, the rate of change is merely too slow to be detected over a short period. Radioactive change is therefore a mono-system change, in which the atom expels a radiant particle, and so undergoes disintegration.

This theoretical interpretation of the experimental results, by which a definite physical conception of each of the stages of the radioactive process is gained, has been justified by its results. Although at the time it was put forward it might have been regarded as somewhat revolutionary, the subsequent developments have been so remarkable that it would probably now be admitted that the disintegration theory offers an intelligible explanation of the known facts with surprisingly little extension of the accepted views on which the physical sciences have been based.

The disintegration series in the case of radium resembles that of thorium closely, except that here there is no intermediate product corresponding to thorium X.[1] The radium atom changes directly into the emanation. For solid compounds of both radium and thorium, but especially in the case of the former, the amount of emanation evolved is a very variable quantity, depending on the state of dryness of the compound, the humidity of the atmosphere, the nature and physical condition of the compound, the temperature, and other conditions. But according to the disintegration theory the amount of emanation should depend only on the quantity of the parent element present. This requirement is in fact fulfilled. The variability of the emanating power observed is merely caused by alterations in the rate of escape of the emanation from the compound into the surrounding atmosphere. If the emanation does not escape into the air, it is found to be present stored up or occluded in the compound, and may be readily obtained from it by heat, or better by dissolving the compound in water. It is found that the emanations escape freely from solutions and show no tendency

[1] Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], **5**, 450.

to remain occluded. Owing to the comparatively slow rate at which the activity of the emanation from radium decays, it tends to accumulate to a marked extent in dry solid preparations, and is instantaneously released into the gas when these are dissolved. This is the explanation of the fact first observed by Giesel,[1] that the activity of radium compounds steadily increases from the time of their preparation, and attains a maximum three to four weeks afterwards nearly four times as great as at first. The activity of radium compounds newly obtained from solution is the non-separable activity, since in solution the emanation readily escapes and carries with it the power of producing the excited activity. The non-separable activity of radium, as in the case of thorium, consists of only 25 per cent. of the α-radiations. On keeping in the solid state, the emanation is reproduced and stored up within the solid compound until equilibrium is produced, the activity of the emanation and of the products of its further change contributing to the total activity of the preparation. The activity therefore steadily rises by an amount corresponding with the activity of the emanation itself, which comprises about 40 per cent. of the total α-radiation, and to the excited activity, which contributes about 35 per cent. of the total α-radiation and the whole of the β- and γ-radiations. If, after equilibrium is reached, the radium compound is dissolved in water, the emanation escapes instantaneously into the gas and carries with it 40 per cent. of the α-activity. If the solution is immediately evaporated to dryness, its activity at first consists of two parts, the non-separable activity and the excited activity due to the active deposit left from the emanation. The excited activity from radium decays fairly rapidly to half the initial value in about 30 minutes, and completely or almost completely disappears in the course of a few hours. But concomitantly a new amount is being produced by the separated emanation, and here, as always, the simple law is followed that the sum total of the activities of the products is always constant and equal to that of the radio-element before separation. Hence the activity of the radium after solution and evaporation decays rapidly, and after five hours consists only of the non-separable activity. The β- and γ-rays have completely disappeared, whilst the α-rays are only 25 per cent. of the initial value. The radiation from the emanation when first separated consists only of α-rays. But when stored in a closed vessel it gradually changes into the active deposit, causing the excited activity, and the latter gives both β- and γ-rays also. Hence the activity of the radium emanation appears to rise rapidly after separation, and after the lapse of five hours the vessel containing it shows β- and γ-radiation to an extent practically equal to that of the original radium compound and α-radiation to the extent of 75 per cent. of the original. If now the emanation is blown out of the vessel

[1] *Wied. Ann.*, 1899, [vi, A], 91.

in which it has been stored, it carries with it 40 per cent. of the total α-radiation, but the whole of the β- and γ-activity and 35 per cent. of the α-activity are left behind on the walls of the vessel (excited activity). In five hours, this will have decayed practically completely, and the emanation, if stored in the meantime in a fresh vessel, will be found to have reproduced there a further crop of the active deposit. This process, however, does not go on indefinitely with any one quantity of the emanation. Its activity, and correspondingly its power of producing the active deposit, slowly decays, attaining half the initial value four days after separation, and disappearing practically completely after three or four weeks. But if at any time the radium from which it was originally obtained is re-examined, it will be found to have again generated a fresh quantity of the emanation. As before, the sum of the emanation separated and of that again accumulating in the radium is a constant. Hence the radium after solution and evaporation slowly recovers its activity, and in three or four weeks the activity reaches again the maximum, and is equal to what it was at first. Radium thus affords an excellent illustration of the changes accompanying radioactivity, and its activity can be separated into three parts, corresponding with that of the parent element and of the first two products of change, by the simple processes of solution, blowing the gas from the solution and storing it in a closed vessel. It also affords valuable evidence of the independence of the α- and β-radiations. The first two changes occur with expulsion of α-rays alone, the β-ray resulting in later changes of the active deposit. In the case of thorium also, it is probable that the β-rays do not result until the matter passes into the active deposit. For uranium, we have the simplest possible case. The whole of the α-radiation results in the first change of the uranium into uranium X, and the whole of the β-radiation in the subsequent change of the latter substance.

It has long been known that the laws regulating the decay of the excited activities from thorium and radium are irregular, and the course of the decay in these cases does not follow a simple geometrical law. In the case of thorium, the excited activity obtained by a short exposure to the emanation rises at first and attains a maximum some hours after the action of the emanation is stopped. It then decays, according to the simple geometrical progression, to half the initial value in 11 hours. In the case of radium, the curves consist of three parts, a very rapid initial decay, a period of slow change, and finally a simple geometrical decrease to half the initial value in 30 minutes. These curves have been the subject of exhaustive investigations by Rutherford,[1] and also by Curie and Danne.[2] The conclusions arrived

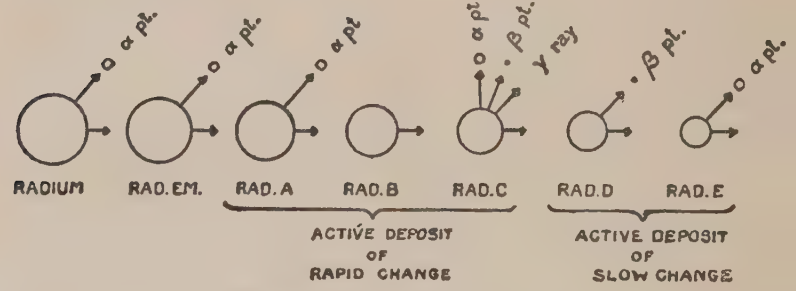
[1] Bakerian Lecture, *Phil. Trans.*, 1904, A, **204**, 213.
[2] *Compt. rend.*, 1903, **136** 364; 1904, **138**, 683, 748.

at by the former are of the highest interest, for they show that the curves can be explained on the view that several successive changes occur in the active deposit after it is formed from the emanation. In the case of thorium, two changes, and in the case of radium no less than five changes, probably occur, the two last in the latter case being of very long period, and not obvious in ordinary circumstances. In the case of actinium, the active deposit from the emanation also probably undergoes two successive changes. Partial separations of the rapidly succeeding products can in some cases be effected by chemical and physical methods, such as volatilisation at high temperature, electrolysis, deposition of the active matter on bismuth, as in Marckwald's work, and solution in acids. Perhaps the point of greatest interest in this elaborate research is the establishment in each case of one change in the disintegration series which proceeds without the expulsion of rays, and which, but for the fact that it is intermediate between changes in which rays are expelled, would have been beyond the means of detection. This discovery opens out a wide field of speculation in its bearing on the general question of the evolution of matter, for it shows that it is quite possible that changes of the same order of magnitude as those occurring, for example, in uranium may be taking place in ordinary inactive matter, but unaccompanied by any recognisable radiation and so beyond the present means of detection.

M. and Mme. Curie[1] observed that the ordinary excited activity of radium does not completely decay, but after falling to about 1/20,000th of its initial value remains sensibly constant at this lower value. This would result if the matter of the active deposit, after passing through the rapid changes which give rise to the ordinary excited activity, enters on a stage where the rate of change is very slow, so that whilst the number of radiant particles expelled in unit time is very small compared with the previous changes, the radioactivity continues over a much longer period before the change is complete. It seems probable that the active material obtained by Mme. Curie from pitchblende and given the name polonium may actually be the slow-changing matter produced from radium after the rapid changes have run their course. For Mme. Curie found that the activity of polonium decays with time, and in about a year after preparation is only half of the initial value. In this, as in other cases, the activity of polonium must be regarded as decaying at the same constant rate whether it is separated from the mineral or not. Hence there must be a continuous production of polonium from the change of one of the radio-elements in pitchblende, and this would be at once accounted for if it were a product of the disintegration of radium. The subject has recently been experimentally investi-

[1] Mme. Curie, *Thesis*, p. 75.

gated by Rutherford,[1] who found that the constant small activity remaining after the complete decay of the ordinary excited activity of radium was due to two successive changes, the first of which is accompanied by the expulsion of β-rays only, and has an estimated period of about 40 years for the change to be half completed. The product of this change gives only α-rays, and has an estimated period of one year. The latter therefore seems to agree very well in properties with polonium. A definite answer to this question cannot be obtained before the rates of change of the two substances have been accurately compared. In view of the extraordinarily complex nature of the later changes occurring in radium, Rutherford has proposed a new and convenient system of nomenclature. The first product of the change of the radium emanation is named radium A, the next radium B, and so on. The following diagram, taken from the paper, illustrates the complete course of transformation of the radium atom.



In the following description, the time in brackets refers to the period in which the preceding change is half completed. Radium passes into the emanation with the expulsion of an α-particle (1000 years, see p. 274). The emanation then changes into radium A with the expulsion of a second α-particle (4 days). Radium A changes into radium B, expelling a third α-particle (3 minutes). Radium B undergoes a rayless change into radium C (21 minutes). Radium C passes into radium D with the expulsion of both α- and β-particles and the emission of γ-rays (28 minutes). Radium A, B, and C constitute the active deposit of rapid change and are the cause of the radium excited activity as ordinarily observed. Radium D passes into radium E with the expulsion of a β-particle only (40 years). Rutherford points out that sufficient radium D must accumulate in pitchblende to constitute a new and sensibly permanent radio-element, and makes the suggestion that the substance obtained by Hoffmann and Strauss [2] from pitch-

[1] *Phil. Mag.*, 1904, [vi], **8**, 636.

[2] *Ber.*, 1901, **34**, 3035.

blende and named by them "radio-lead" may have owed its activity to the presence of radium D. Radium E expels an α-particle (1 year) and passes into matter which is either completely inactive or changing so slowly that no activity has yet been observed. Radium E corresponds well in nature with polonium.

An important advance in our knowledge of the α-rays of radium, which bears out in a striking and novel manner the theory of the successive changes occurring in radium, has recently been made by Bragg.[1] The results obtained are, in addition, of considerable theoretical interest. In this work, an ionisation chamber was employed consisting of two parallel metal surfaces between which the ionisation could be measured, the lower surface being made of gauze to allow of the free passage of the α-rays into the chamber. It was gradually brought from a distance on to a plate on which a solution of a radium salt had been evaporated, and the ionisation measured at various distances from the radium. Mme. Curie showed with a somewhat similar arrangement that the ionisation produced by the rays from polonium extended into the gas a well-defined distance from the polonium and then ended abruptly, so that just within this distance a large ionisation was observed, and just without practically none. In the case of radium, it was found, on bringing the ionisation chamber successively nearer to the radium, that several sudden increases in the amount of ionisation occurred, pointing to the existence of several kinds of α-rays, each with a definite penetrative power. By subjecting the radium to processes, similar to those described, whereby it could be freed from the emanation or from the emanation and the active deposit produced from the emanation, Bragg succeeded in eliminating the α-rays from these products and in analysing the total radiation into three groups. The most penetrating rays extended to a distance of about 6·2 cm. from the radium in air. These, as he showed, belonged to radium C, adopting the new nomenclature. If the ionisation near the radium is 100, this ionisation equalled about 25. From 6·2 to 4·6 cm., the amount of ionisation remained constant. From 4·6 to 3·8 cm., the ionisation increased to nearly treble of that at 6 cm., or 75 per cent. of the total, the α-rays from both the radium A and the emanation causing the increase. These two types are of nearly equal penetrative power, but distinct evidence of two separate sets was obtained. From 3·6 to 3·2 cm. no increase occurred, and at the latter distance a further sudden increase to about four times the initial ionisation at 6 cm. took place. The last was due to the 25 per cent. of the total radiation comprising the non-separable activity. From 3·2 cm., the ionisation remained constant right up to the surface of the radium. Thus, each

[1] Bragg, *Phil. Mag.*, 1904, [vi], 719; Bragg and Kleeman, *ibid.*, 726.

α-particle in the disintegration series of radium is expelled at a certain definite velocity and is capable of penetrating a certain definite distance of air before losing its power of ionising. The α-particle from the radium atom is expelled at a lower velocity than the α-particle from the emanation atom, and the latter at a lower velocity than that from radium C, but all the α-particles from each kind of matter are expelled at the same definite velocity. Thus, the Daltonian conception that the atoms of the same element are all exactly alike applies even to the velocity with which they expel radiant particles on disintegration. This is probably the most severe experimental test to which this conception has ever been subjected, for it might be imagined hardly possible for any two systems, so extraordinarily complex as the heavy atoms are known to be, to be so absolutely alike that exactly the same velocity should be impressed in each case on the fragments during their explosive disruption.

In the developments of the last two years, abundant evidence has been forthcoming for the view that radioactivity is the result of changes in matter of a more fundamental character than those hitherto studied. From the point of view that radioactivity is *accompanied* by change, it follows that the final product or products of the changes cannot be radioactive, and must therefore be completely beyond the range of detection in ordinary circumstances. On the other hand, since these final products must have been steadily accumulating throughout past epochs, they must exist in sufficient quantity to be recognisable in the natural minerals in which the radioactive elements exist, unless they succeed in escaping in some way from them. Since these minerals have been long studied, it may be further stated that the final products of radioactive change are probably well known elements. A review of the composition of the radioactive minerals from this point of view led Rutherford and Soddy[1] to make the suggestion that helium was probably the product of radioactive changes. The evidence rested on the inability of helium to enter into combination, or to be condensed in any way by cold or pressure or chemical attraction. So that its presence in comparatively large volume in natural minerals was in itself remarkable. Further, Sir William Ramsay had drawn attention to a fact which, since the discovery of radioactivity, assumed a new significance, that helium is only found in minerals which contain uranium or thorium, that is, which are radioactive. In addition, the state in which helium occurs in minerals is exactly analogous to the state in which the emanations, when they do not escape, are retained by solid compounds. In both cases, the gases may be removed by heat or solution, but do not show the least tendency

[1] *Phil. Mag.*, 1903, [vi], **5**, 579.

to be reabsorbed by the solids from which they are obtained. It seemed likely that in each case, the gas being formed throughout the mass of the solid, it was mechanically imprisoned within the interior, and so unable to escape. The direct proof of this view was obtained by Ramsay and Soddy,[1] who established that there is a continuous production of helium from radium in sufficient quantity to be directly recognised by the spectroscope. A few milligrams of radium bromide that had been kept some months in the solid state were dissolved in air-free water *in vacuo*, and the gases liberated were freed from the hydrogen and oxygen which are known to be produced by the decomposition of the water by the radium, by means of a glowing, partially oxidised copper spiral. Water was removed by phosphoric oxide and the radium emanation by cooling with liquid air. The residue as shown by its spectrum proved to be practically pure helium. The radium emanation that had been condensed out in this experiment was by suitable arrangements introduced into a second completely exhausted spectrum tube, which was then sealed. In this experiment, precautions were taken to remove helium if present, by admitting hydrogen, while the emanation was condensed, and again exhausting. Three days after the tube had been sealed, the D_3 line of the helium spectrum made its appearance, and later the whole of the spectrum was observed. This experiment was repeated many times with the same quantity of radium, by the simple process of waiting between the experiments a sufficient time for the emanation to be reproduced by the radium. The latter was kept in solution untouched, and the gases accumulating removed from time to time by a mercury pump. As the emanation was changing and producing helium within the spectrum tube, a fresh quantity of emanation was being regenerated by the radium, and this process goes on indefinitely, the radium being transformed into helium through the emanation.

The helium obtained in the first experiment must have been derived at least in part from the change of the emanation occluded by the solid compound. There is no experimental evidence as yet available to show whether helium is not also being produced in the first change of the radium as well as in the later change of the emanation. Rutherford favours the view on general grounds that the α-particle is an atom of helium, and this involves the consequence that helium is a product in all cases of α-radioactivity, not only in radium, but also in all the other radio-elements. Strutt has drawn attention to the fact that the mineral monazite which contains a fair quantity of helium contains thorium but no radium.

It is by no means probable that helium is the sole product of

[1] *Proc. Roy. Soc.* 1903, **72**, 204.

the changes occurring in radium. In fact, the evidence of the final slow changes show that it cannot be the ultimate product in the sense of being the last state that the successively disintegrating atom assumes, but is, if not the α-particle, certainly a by-product produced simultaneously with one or more of the intermediate products.

The reasons are many why helium is so far the only product that has been detected. In the first place, it is the only one that has been specifically looked for. The evidence which led to the prediction of its origin could only apply to a rare inert form of matter. Secondly, helium can probably be detected in as minute amount as any of the non-radioactive elements. Thirdly, being uncondensable, it can readily be separated from large amounts of all other gases. Lastly, its great rarity and absence from the common materials and reagents of the laboratory make the evidence of its presence unequivocal. To establish beyond question the production of any of the commoner elements from radium with the quantity of the latter at present available, would be a difficult experimental task.

The production of helium within a sealed quartz tube containing radium which had been fused and the tube completely exhausted before sealing has been shown by Curie, Dewar, and Deslandres. In a photograph of the spectrum taken twenty days afterwards, by passing a discharge through the tube by means of external electrodes, the helium spectrum was plainly visible.

Himstedt and Meyer [1] sealed 25 milligrams of radium bromide in a small U-tube provided with electrodes, filled it ten times with hydrogen and exhausted, and finally sealed it when completely exhausted. They observed the appearance of the helium spectrum after three months. A similar quantity of radium was converted into sulphate and heated for a long time to a very high temperature in a quartz tube. During the process the tube was filled with hydrogen many times and again exhausted completely before it was sealed. The growth of the helium spectrum was again observed after a period of three weeks. They conclude that unless it is supposed that in spite of the long and repeated ignition and exhaustion, helium still remained occluded, the only explanation is that new helium is in fact arising from the radium preparation.

Simultaneously with these discoveries, advances no less important have been made in our knowledge of the energy changes occurring in radioactive substances, again by the use of ordinary methods of investigation. Giesel [2] found that a solution of a radium salt in water continuously disengages hydrogen and oxygen in considerable quantity, the hydrogen being in slight excess of the combining proportion. From

[1] *Ann. Physik.*, 1904, [iv], 15, 184. [2] *Ber.*, 1903, 36, 347.

measurements by Ramsay and Soddy,[1] 10 c.c. of the mixed gases are evolved per gram of radium per day over a period of many months without diminution. This represents an energy expenditure of 20 calories daily. In spite of every precaution taken to avoid the presence of oxidisable matter, the hydrogen was always present in slight excess of the combining proportion. This remarkable fact has received no adequate explanation.

Curie and Laborde[2] measured the energy of the radioactive change in radium directly by the heat evolved in a given time from a known quantity of radium within a Bunsen's ice calorimeter. Their result that 1 gram of radium evolves 100 calories every hour has been repeatedly confirmed. Next, Rutherford and Barnes[3] analysed the heat development and determined the fraction developed at each successive change in the disintegration series. On the disintegration theory, the intensity of the α-radiation is a measure of the number of atoms disintegrating, and each disintegration accompanied by the expulsion of an α-particle was found to evolve a similar amount of heat. On removing the emanation by heating from a quantity of radium which had attained its maximum activity, the evolution of heat immediately decreases, and in the course of a few hours, after the α-activity had fallen to 25 per cent. of the initial, the heat effect had diminished correspondingly, and was only about a quarter as great as at first. The emanation removed was condensed in a small glass tube by liquid air. It was found to give out heat exactly to the extent that the heat evolution from the radium had diminished, and after a few hours gave three times as much heat as then given by the radium, or three-quarters of the total. As the emanation was reproduced by the radium, the heat evolution of the latter increased, whereas as the activity of the emanation decayed its heat evolution decreased correspondingly. The sum total of the two heat evolutions was at all times a constant, and equal to that originally given by the radium before the removal of the emanation. Hence the emanation from 1 gram of radium present in the condition of radioactive equilibrium, together with the products of the further change of the emanation, evolve 75 calories per hour. The integral of the continuously diminishing quantities of heat evolved from the emanation before its activity is exhausted is given by Q/λ, where Q is the heat evolved per second initially and λ is the radioactive constant, or proportion of the emanation changing per second. $Q/\lambda = 10{,}540$ calories.

Ramsay and Soddy[4] measured the actual volume occupied by the equilibrium quantity of emanation from a known weight of radium under normal temperature and pressure. This was effected in a very

[1] *Proc. Roy. Soc.*, 1904, **73**, 346. [2] *Compt. rend.*, 1903, **136**, 673.
[3] *Phil. Mag.*, 1904, [vi], **1**, 202. [4] *Proc. Roy. Soc.*, 1904, **13**, 346.

narrow thermometer tube, into which the emanation, after it had been freed from other gases by condensation, was compressed by means of mercury. They concluded that the equilibrium quantity of emanation from 1 gram of radium occupies a volume not greater than 1·3 cubic millimetres at normal temperature and pressure.

From the three preceding results, the conclusion follows that 1·3 cubic millimetres of emanation evolve 75 calories per hour, and that 10,540 calories are evolved during the course of its complete change. This is a quantity of energy four million times greater than is evolved by the same volume of hydrogen and oxygen when they explode to form water. *This is a completely experimental result*, and is independent of any theoretical interpretation which may be put upon it. It is probably the most far-reaching and revolutionising fact that has yet transpired in the study of the radioactive substances. This enormous evolution of energy which accompanies the production of helium from the radium emanation establishes beyond question the new and fundamental character of radioactive change. It may be noted and pointed out that this fact alone negatives the suggestion that the energy of radioactive substances is derived from the outside. It has been suggested, for example, that all space is traversed by undiscovered radiations to which ordinary matter is completely transparent, but to which the radioactive substances are opaque. On this view, the energy traversing a cubic centimetre of space must be at least 60,000 calories per hour. The total quantity in the universe must therefore be so great that the hypothesis involves far greater difficulties than the facts it is designed to explain. The decay of the activity of the emanation and its concomitant reproduction by the radium are even stronger arguments against the view.

From the volume of the emanation produced per second from a known weight of radium, Ramsay and Soddy [1] calculated the proportion of the radium changing per second, that is, the radioactive constant of radium. They deduced that about 1/1150th part of the radium changes every year. A similar result has been theoretically deduced by Rutherford from the energy evolved from radium, and the energy of the α-particle as calculated from its mass and velocity. The comparatively rapid rate at which radium undergoes disintegration shows clearly that the element must be being reproduced by some means in the minerals containing it. In 1903, Rutherford and Soddy [2] put forward the view that it was probably a product of the disintegration of uranium. This question has not yet been definitely settled.

Ramsay and Collie,[3] using methods similar to those employed in the

[1] *Proc. Roy. Soc.*, 1904, **73**, 346.
[2] *Phil. Mag.*, 1903, [vi], **5**, 590.
[3] *Proc. Roy. Soc.*, 1904, **73**, 470.

experiments on the production of helium from the emanation, have succeeded in showing that the emanation before it changes into helium possesses a definite and characteristic spectrum, which was mapped. Sir William and Lady Huggins[1] have photographed the spectrum of the fluorescent light of radium in air, and shown that it consists of the negative glow spectrum of nitrogen. According to Crookes and Dewar, unless nitrogen is present in the atmosphere only a continuous spectrum is obtained. This was found to be the case in an atmosphere of helium, and also in a vacuum.

The rate of change of the elements uranium and thorium may be calculated from the rate of change of radium by comparing the α-radioactivity and the number of changes in which α-particles are evolved in each case. The best determinations of the activity of the purest preparations of radium show that this element possesses about two million times the α-activity of uranium or thorium, which in this respect are very nearly equal. In thorium, the same number of changes cause the α-activity as in radium in the circumstances in which the activity is usually measured. The rate of change of thorium is therefore about 5×10^{-10} per year. In uranium, only one change is known, and the rate of change is therefore about 2×10^{-9} per year.

In the following table, the unstable elements at present recognised have been arranged in the order of their instability. In the first column, the radioactive constants, as defined by the proportion changing per second, and in the second column the average lives are given:

	λ (sec.)$^{-1}$.	Average life.
Actinium emanation	$1{\cdot}87 \times 10^{-1}$	5·8 seconds
Thorium emanation	$1{\cdot}15 \times 10^{-2}$	87 ,,
Actinium B	$7{\cdot}7 \times 10^{-3}$	130 ,,
Radium A	$3{\cdot}8 \times 10^{-3}$	264 ,,
Radium B	$5{\cdot}38 \times 10^{-4}$	31 minutes
Radium C	$4{\cdot}13 \times 10^{-4}$	40 ,,
Actinium A	$2{\cdot}80 \times 10^{-4}$	60 ,,
Thorium B	$2{\cdot}10 \times 10^{-4}$	79 ,,
Thorium A	$1{\cdot}75 \times 10^{-5}$	16 hours
Radium emanation	$2{\cdot}0 \times 10^{-6}$	5 days, 19 hours
Thorium X	$2{\cdot}0 \times 10^{-6}$	5 ,, 19 ,,
Uranium X	$3{\cdot}6 \times 10^{-7}$	32 ,,
Radium E	—	about 18 months
Radium D	—	,, 60 years
Actinium	—	—
Radium	$3{\cdot}0 \times 10^{-11}$	1,150 years
Uranium	$6{\cdot}0 \times 10^{-17}$	5×10^{8} ,,
Thorium	$1{\cdot}5 \times 10^{-17}$	2×10^{9} ,,

It will be seen that a wide range of stability is represented between limits of a few seconds on the one hand and cosmical epochs on the other. The question whether there may not be an opposite process in nature, as yet undiscovered, whereby the parent elements themselves

[1] *Proc. Roy. Soc.*, 1903, **72**, 196 and 409.

are being reconstructed, and their quantity maintained, was discussed by the author in a recent paper.[1] One of the most interesting results of the study of radioactive change is that it reveals the possibility of a slow continuous evolution of the elements, such as has frequently been suggested, without in any way subverting or altering the foundations on which the present evidence of the conservation of the elements rests. The idea of a gradual conversion of one elementary form of matter into another is opposed to chemical evidence, for fractional methods should have revealed the existence of such a process. Radioactivity has brought to light a type of change which, whilst of any degree of slowness, so far as the mass of matter is concerned, is sudden for the individual particle. Since the rates of change appear to be constant and invariable in all circumstances, it follows that no type of matter intermediate between the parent element and final product can accumulate in sufficient quantity to come within range of direct detection if it is changing faster than a very slow rate. The rapidity of change as measured by the degree of radioactivity must be inversely proportional to the quantity capable of existence at one time. The experimental results, so far as they are available, show that the quantities of uranium, radium, and polonium in pitchblende are as $10^9 : 10^3 : 1$, and these ratios are of the same order as the relative activity or rates of change. We have here the introduction into chemistry of a conception analogous to that of evolution in the biological sciences. The existing state of matter and the present composition of the earth must be regarded as the direct consequence of past occurrences. The periodic table becomes indicative of the forms of atomic structure that are stable, rather than of those that are possible. The question why the majority of the atomic weights approximate to multiples of hydrogen still remains without explanation, but it has been put on an entirely new basis; for of the eighteen forms of matter given in the preceding table only the last three are assigned places in the periodic table, and it seems probable that forms of matter intermediate between the members of that table are not known only because they cannot survive. From this point of view, there are no longer any grounds for believing, as in Prout's hypothesis, that the approximation of the atomic weights to whole numbers argues in favour of a step by step condensation of matter, by units equal to the hydrogen atom. The periodic law represents a periodic variation in stability with mass in which the positions of maximum stability correspond to multiples of the mass of the hydrogen atom in the greater number of cases, but the reason for the periodicity of stability remains to be elucidated.

An important argument may be drawn from the fact that in

[1] *Mem. Manchester Phil. Soc.*, 1904, **48**, ii, Wilde Lecture.

the stars few if any forms of matter not existing on the earth are found, for this must point to the conclusion that the law developed from the study of radioactive change, that atomic stability is independent of external conditions, holds universally over much wider ranges of temperature and under conditions other than those for which it has been experimentally verified. Sir Norman Lockyer's [1] theory is of more than usual interest in the present connection, as it was based primarily on accurate astronomical data. It seems that the main fact on which this theory was based is in strong agreement with recent developments. Lockyer found that the temperature of a star appears to be in inverse ratio to the complexity of its composition, so that if the stars are classified in order of descending temperature the hottest give spectra corresponding to the lightest elements only, the heavier elements gradually making their appearance in increasing numbers with decreasing temperature. This is in agreement with the fact that a heavy element is resolved with the evolution of an enormous amount of energy. But it is now clear that if the process which Lockyer imagined occurred, and the light elements condensed into the heavy ones, so great an absorption of energy must follow that the heat of the star on cooling would represent only an insignificant fraction of that required. So that it seems more justifiable to assume that in the stars, as in the earth, evolution is proceeding from the heavy towards the lighter forms.

In conclusion, it may not perhaps be out of place to call attention to some considerations attracting great attention among physicists, which although hardly yet within the scope of chemistry, may exert a profound influence in the future. The discovery of the corpuscular types of radiation, firstly the cathode rays and now the α- and β-rays, has given great support to the modern view of the nature of electricity. This view has been happily called the atomic theory of electricity, to distinguish it from the older fluid theories. Faraday's law of electrolysis suggested the conception of the unit or atomic charge of electricity possessing the same qualities of invariability and indivisibility as the material atom. The development of the electromagnetic theory of light, and its establishment after the researches of Hertz, effected the further removal of the dividing line between electricity and matter by showing that the electric charge possesses a certain inertia, or mass. The magnetic field created in the ether by the motion of an electric charge and which for ordinary speeds is proportional in intensity to the velocity of the charge, represents a certain store of energy in the medium. So that an electric charge resists alteration of velocity or possesses inertia, indistinguishable from that possessed by matter. For similar charges, the value of the electric

[1] *Inorganic Evolution*, 1900.

inertia increases with the concentration of the charge. On the older fluid view of electricity, in which even in the case of single atoms the charge was supposed to be uniformly distributed over the surface according to the ordinary laws of electrostatics, the conception of electrical inertia remained of no more than abstract interest. For even in the case of the hydrogen ion, the most intensely charged form of matter known, the charge is too diffused for its inertia to be comparable with that of the uncharged atom. With Professor J. J. Thomson's elucidation of the nature of the cathode rays, and his determination of the mass of the cathode-ray corpuscle, the property of electrical inertia at once assumed extraordinary practical interest. The extremely small size of the corpuscle as evidenced both by the value found for its mass and its power of penetrating ordinary solid matter, made it appear probable that it was the atom of electricity, or electron, dissociated from matter. For this to be the case Thomson has calculated that the charge must be concentrated within a sphere of diameter one hundred-thousandth of that usually assigned to the diameter of the molecule.[1] The observed mass, namely, about one-thousandth of the hydrogen atom, would then be of purely electro-magnetic origin and an attribute of the charge. In this sense, the electron has been recognised by Larmor and others as a possible basis of matter, the various atoms being systems composed of the requisite number of discrete electrons in stable groupings to give a total mass equal to the atomic mass. In this way, all material and mechanical phenomena would possess ultimately an electromagnetic origin. Such a view differs in one fundamental point from the older ideas, and it has fortunately been found possible to obtain in the case of radium something of the nature of a crucial test by actual experiment between the rival views. Although for ordinary speeds, such as those dealt with in mechanics, chemistry, or physics, the electrical inertia of an electron remains constant, it was deduced in 1881 from the electromagnetic theory of light by Heaviside, that the inertia of the electron must increase when the velocity of light is approached, and at that velocity become infinite. In the case of the β-rays of radium, Kaufmann[2] has shown that the most penetrating rays consist of electrons travelling with a speed of 95 per cent. of that of light. At this speed, the mass of the electron, if it is entirely of electromagnetic origin, should be considerably greater than the normal value found in the case of the cathode-rays or the slower moving β-rays of radium. Kaufmann showed that the ratio of the charge to the mass of the electron continuously decreases as the velocity increases, and for the fastest moving electrons is only two-fifths of the ordinary value. **J. J.**

[1] J. J. Thomson, *Electricity and Matter*, 1904.
[2] *Compt. rend.*, 1902, 135 577.

Thomson[1] has shown that these results are in good accordance with the theoretical values deduced from the assumption that the mass is entirely electromagnetic. As this is the only case in which any variation has been observed in the ratio of the charge to the mass of the electron, although a considerable number of cases have been examined, and as the result was definitely predicted from the electromagnetic theory, it furnishes a very strong argument in favour of the new views. If they are accepted they lead directly to the result that the law of the conservation of mass can only have a limited application. In mechanical and chemical phenomena, matter travelling with velocities of the order of that of light is unknown, and the law therefore applies rigidly. But in radioactive change it should not apply. If, as appears certain, the energy of radioactive change is derived from the internal energy of the atomic structure, the constituent electrons or potential α-particles which go to make up the atom must be permanently in extremely rapid orbital or oscillatory motion, approaching in some cases to that of the velocity of light. For it is recognised that the velocity with which the radiant particles are expelled are too great to have been suddenly produced by the action of any known force. The constituent electrons of a radium atom must therefore vary in mass according to their velocity. On the new views, no simple numerical relations should exist between the atomic weights, for the latter are to a certain extent a most complex function of the internal energy of the atom. On disintegration, the expelled electrons, on encountering obstacles, are absorbed and stopped, so that in the case of the faster moving electrons a diminution of mass must simultaneously occur. Hence the products of the disintegration of radium must possess a total mass less than that originally possessed by the radium, and a part of the energy evolved must be considered as being derived from the change of a part of the mass into energy. In future, it may be possible to put this revolutionary deduction to the test of direct experiment. As, however, the loss of weight in radium under conditions in which the expelled electrons escape freely from the system is so small that it has not yet been detected, it is likely that a considerable time must elapse before enough radium is available for the experiment. But there is no doubt that it is only a question of time before it becomes possible for even these fundamental conclusions, arising out of what but a short time ago was one of the most abstract regions of physics, to be put to the actual test of crucial experiments in the laboratory.

The year 1904 witnessed the appearance and the successful completion of the first year of existence of a new quarterly journal, *Der*

[1] *Conduction of Electricity through Gases*, 1903, 535.

Jahrbuch der Radioaktivität und Electronik, under the able direction of Prof. J. Stark, of Göttingen. The journal has already justified its existence, if only by the publication of a complete and carefully classified catalogue of all the literature dealing with these subjects, from their beginning right up to the end of the year that has just closed. It is a pleasure, in acknowledging the assistance derived from this catalogue in the preparation of this report, to wish the new journal a long continued career of usefulness.

FREDERICK SODDY.

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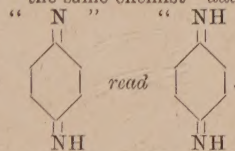
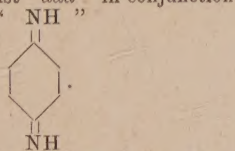
20	1*	*for*	"water" *read* "alcohol."
56	24	,,	"$R_2>O<^{X}_{Mg}$" *read* "$Et_2>O<^{X}_{MgR}$."
57	8*	,,	"$R{\cdot}C{<}^{O}_{H}$" *read* "$R{\cdot}C{<}^{O}_{OH}$"
67	12*	,,	"saccharic" *read* "saccharinic."
67	19*	,,	"parasaccharic" *read* "parasaccharinic."
69	3*	,,	"*iso*saccharic" *read* "*iso*saccharinic."
103	3	,,	"$CH_3{\cdot}O{\cdot}COCH_3$ / $C{\cdot}CO_2{\cdot}C_2H_5$" *read* "$CH_3{\cdot}O{\cdot}CO{\cdot}CH_3$ / $CH{\cdot}CO_2{\cdot}C_2H_5$"
114	3	*after*	"the same chemist" *add* "in conjunction with J. F. Thorpe."
122	19	*for*	 *read* 
136	18	,,	"Morrell and Bellars" *read* "Morrell and Hanson."
229	16*	,,	"Lingren" *read* "Lindgren."
230	15	,,	,, ,, ,,
232	9*	,,	"Mitchell City" *read* "Mitchell Co., N.C."
235	4	,,	"Pala, San Diego Co." *read* "Campo sea, Calaveras Co."
235	6	,,	"*Clandetite*" read "*Claudetite.*"
235	23	,,	"California" *read* "Colorado."
235	7*	,,	"Ytterbia" *read* "Ytterby."
236	15*	,,	"Davies" *read* "Davis."
238	19	,,	"Vrendenburg" *read* "Vredenburg."
273	footnote	,,	"73" *read* "13."
279	18	,,	"velocity" *read* "velocities."

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